Letter to the Editor:

Dear Editor,

We would like to thank the two reviewers for their careful reading and constructive comments. We have revised the manuscript, incorporating the comments from the two reviewers, as noted in the two documents submitted.

Thank you again for your consideration.

Best regards,
Luisa Molina

Anonymous Referee #1

General comments

Description: This discussion paper describes emission factors of diesel-powered trucks and buses in Mexico City measured using both the Aerodyne mobile laboratory and on-road remote sensing. The targeted compounds include CO, NOx, SO2, selected VOCs, PM, black carbon (BC), and particulate organic carbon (OC). The two methods produced similar results. BC emission factors were consistent with those measured in other studies, while the OC/BC ratio was larger than found in California. Emission factors generally agreed with those used in the EPA MOVES-2014b model for NOx and BC and were higher for CO, OC, and selected VOCs.

Relevance:

Heavy duty diesel-powered vehicles are responsible for substantial amounts of BC and NOx emissions, yet there are limited on-road measurements of emissions from these vehicles. This work adds to the database of such measurements and shows that the chasing method with a mobile lab and the on-road remote sensing method produce comparable results, so it is fair to synthesize results across these different types of studies.

Assessment: The work contributes useful information about emissions from diesel engines. The writing and figures are very clear and informative. The paper illustrates the strengths and weaknesses of each of the two methods for measuring emission factors. The paper could be strengthened through some reorganization of the Results and Discussion and addition of statistical tests.

We thank the reviewer for the constructive comments on the paper.

Specific comments

1. p. 4, line 10: A little more information about the prescribed driving routes and operation of the vehicles would be useful. What was the range of speeds? Were the engines always warmed up beforehand?

We thank the reviewer for this suggestion as this will allow the results to be more adequately compared to future studies of emission characteristics of diesel vehicles in Mexico. We have now included a more detailed description of the driving conditions (the range of speeds and accelerations of the vehicle sampled) during the tests in the supplemental material document.

2. p. 7, lines 24-26: "Since the measurements were obtained in similar prescribed driving routes, the results show a wide range of average emission factors associated with each vehicle engine and emission control characteristics." The wording and logic are not quite right here. I think the authors intend to emphasize that driving conditions were very similar for all vehicles, so differences must reflect variability

between engines and control systems. But later, they assert that there is large variability even for the same vehicle.

We thank the reviewer for calling our attention to this ill-constructed phrase. As pointed out, we want to emphasize that the driving conditions were very similar for all vehicles. We have modified the paragraph accordingly:

"Since the measurements were obtained under similar prescribed driving routes, differences in results mainly reflect variability among vehicle engines and emission control characteristics."

As stated, the results indicate that even after controlling for driving routes the observed variability of emission factors still can be large. This is in agreement with current understanding of real-world emissions as compared to laboratory-based studies and the growing acknowledgment that engine performance can produce large variability under real-world operation conditions.

3. p. 8, line 7: The comparison of emission factors among different vehicle types begs for statistical tests of differences. This is true for the presentation of differences by control technology, too.

We thank the reviewer for this valuable suggestion. We have now performed statistical testing for the significance of the results between vehicle types, by control technology, and between measurement techniques.

We have analyzed the statistical significance between control technologies for $PM_{2.5}$ EF using non-paired non-parametric Wilcoxon Rank tests and found that with a 95% confidence level the results for the EPA98 and EPA04 are significantly different. Similarly, differences between EURO3, EURO4, and EURO5 EF were found to be significantly different with a 95% confidence level. However, the rest of the tests indicated that the results for the EPA98 and the EURO3 (the older technologies sampled) were not significantly different with a 95% confidence level. Therefore, the following paragraph has been included in the text:

"Non-paired Wilcoxon Rank tests indicate that there is statistically significant difference (at the 0.05 significance level) between the $PM_{2.5}$ emission factors obtained for the EPA98 and EPA04 control technologies as well as among the EURO3, EURO4, and EURO5 technologies. However, the results for the EPA98 and the EURO3 technologies were not significantly different."

We similarly performed non-paired Wilcoxon Rank tests for comparing the emission factors by vehicle type for each pollutant. We found that CO, NO_x, and SO_2 from service trucks, urban buses, and Metrobuses were significantly different among them, whereas their VOCs measured (C_2H_2, acetaldehyde, benzene, toluene, C2-benzenes), and PM components (BC, OC, and inorganics) were not statistically significantly different. On the contrary, VOCs and PM-components emission factors obtained from Turibuses were statistically different from the corresponding emission factors from service trucks, urban buses, and Metrobuses. Thus we have included the following paragraph:

"Non-paired Wilcoxon Rank test indicate that there is statistically significant difference (at the 0.05 significance level) between emission factors from service trucks, urban buses, and Metrobuses for the CO, NO_x, and SO_2 pollutants, whereas their corresponding VOCs, BC, OC, and PM-inorganic emission factors were not significantly different. VOCs, BC, and PM-inorganic emission factors from biodiesel-fueled Turibuses were significantly different from the corresponding emission factors from service trucks, urban buses, and Metrobuses."

In addition to the analysis suggested by the reviewer we also evaluated the statistical significance of the results for CO and NO emission factors that were obtained with both the chasing and the remote sensing techniques. Since these represent co-sampled data we used paired t-test with a 0.05 significance level. The results indicate that in both cases of CO and NO co-samplings there is no significant difference between the results obtained by the two measurement techniques, with a confidence level of 95%. Therefore, we have now added the following paragraphs to the results:

"Paired t-tests indicate that there is no statistical significant difference (at the 0.05 significance level) between the two measurement techniques for both cases of CO and NO emission factors."

4. p. 8, line 26: The paragraph about the limitations of the sample size should be moved to the Discussion section.

As suggested by the reviewer, we have moved the discussion on the limitations of the sample size to the Discussion section.

5. p. 9, line 5: The comparison between the two methods in Section 4.1 seems it belongs more in the Results section than in the Discussion section because it is a straightforward presentation of results that address one of the objectives of the study.

We have moved the comparison of the two methods to the Results section.

6. p. 9, line 11: For comparison of the two methods, the authors chose to use the 10 seconds of AML data leading up the instant of remote sensing, which lasted 1 second. Why not isolate the 1-2 seconds of AML data that best correspond to when the remote sensing measurement was captured?

For the estimation of the emission factors using the chasing technique, the second-by-second measurements are integrated over a time period to account for the dispersion of the emission plume. Thus, if too few data points are included in the integration the resulting emission factor may not properly reflect the plume development and unnecessary uncertainty is introduced in the analysis. Based on our past experience with data analysis of this technique, we consider a good conservative

number of data points for plume development is about 10 seconds as the basis for the choice of integration time. Thus, we have now complemented the following sentence:

“Since the remote sensing technique measures the emission factor of the sampled vehicle only while it passes through the detectors, only the emission factors obtained with the mobile laboratory ~10 seconds before and up to the corresponding actual moment of co-sampling with the remote sensing detector were considered for the comparison between the two techniques. Thus, we assume that a time period of 10 seconds is sufficient to capture a large portion of the emission plume sampled by the mobile laboratory.”

7. p. 11, line 15: I assume that all the vehicles tested in this study were running on petroleum diesel, so results for B10 and B20 biodiesel are irrelevant to the present study and do not merit mention here, or they require greater justification for inclusion in the comparison.

In the discussion section of the paper we compare our results on the emission factors from biodiesel vehicles to the only other available literature study of similar measurements in Mexico that used B10 and B20 blends. We believe that, given the very limited information currently available, the comparison information and discussion presented is a valuable addition and thus we have decided to keep it in the manuscript.

8. p. 12, line 10: Can the authors comment on why there are differences in the OC/BC ratio compared to that found in other studies? Might altitude explain some of it or dilution? The mobile lab and remote sensing detect fresher, less diluted plumes compared to tunnel studies.

There are several possible reasons why the results show higher OC/BC ratios in comparison to other studies. These include differences in conditions derived from the environment (e.g., altitude, temperature), technical sampling methods (capturing fresh versus more diluted emissions), and diesel fuel composition. Unfortunately it is not possible from our results to quantitatively assess the contributions from these factors as it is beyond the scope of this study. Dedicated experiments controlling for these factors as well as vehicle technology and driving conditions could help to quantify the impacts of these factors. Nevertheless, it is possible to argue that the higher OC/BC content in the Mexican results obtained with the mobile laboratory are not due to differences in the sampling technique used in tunnel studies. As the reviewer pointed out, the former capture more fresh emissions than tunnel studies and, therefore, secondary formation of organic aerosols in the air masses would only increase the OC/BC during in the tunnel study sampling (Massoli et al., 2012), which is in the opposite direction needed to explain the observed differences.

No samples were obtained in our study of the diesel fuel employed, and thus it is not possible to know its exact organic chemical composition and its effects on emissions. Although a detailed chemical composition of diesel fuel by PEMEX (Mexican National Oil Company) is not publicly available, an official

report indicates a predominant fraction of paraffin compounds of linear molecular chains with 11 to 12 carbons and a maximum 30% (in volume) of aromatics (IMP, 2014). In principle, a dedicated experiment could be set up to investigate the effects of OC formation due to differences in PEMEX's diesel fuel composition, but this is beyond the scope of this study. We have therefore included the following paragraph:

"Several factors including driving conditions, vehicle technology, and diesel fuel composition can contribute to the observed differences, but the quantification of these contributions is beyond the scope of this study. Nevertheless, the higher organic content of the emissions in the sampled Mexican vehicles with respect to those measured in California by Dallman et al., (2014) illustrate the large emission differences in PM composition that can be found in diesel fleets around the world, thus further indicating the need for locally adjusting the emission factors databases in mobile emission models."

References:

IMP, Instituto Mexicano del Petroleo: Factores de Emision para los diferentes tipos de combustibles fosiles que se consumen en Mexico. Informe Tecnico F.61157.02.005. Dirección de Servicios de Ingeniería Gerencia de Servicios en Ingeniería Región Centro-Norte. 2014. Available: http://www.inecc.gob.mx/descargas/cclimatico/2014_inf_parc_tipos_comb_fosiles.pdf

Paola Massoli , Edward C. Fortner , Manjula R. Canagaratna , Leah R. Williams , Qi Zhang , Yele Sun , James J. Schwab , Achim Trimborn , Timothy B. Onasch , Kenneth L. Demerjian , Charles E. Kolb , Douglas R. Worsnop & John T. Jayne (2012) Pollution Gradients and Chemical Characterization of Particulate Matter from Vehicular Traffic near Major Roadways: Results from the 2009 Queens College Air Quality Study in NYC, Aerosol Science and Technology, 46:11, 1201-1218, DOI: 10.1080/02786826.2012.701784.

9. Table 2: This could be moved to the supplemental information, as a more digestible summary of the results appears in the figures. Footnote 4 mentions "hundredths" of Metrobuses. Should this be 101 Metrobuses, the number sampled?

We agree that the information shown in Table 2 is somewhat dense. However, we believe it is important to present directly in the main manuscript a summary table of the average results obtained with both techniques. Therefore, we have decided to maintain Table 2 in the main text of the manuscript.

We thank the reviewer for the suggested edit on the footnote 4, the change has been made.

10. Figure 4: The NO figure shows small variability in mobile lab measurements and much larger variability in remote sensing measurements (large spread in the y-axis direction). This does not comport

with Fig. 1, which shows similar variability in the NO emission factors measured by both the mobile lab and remote sensing. Is it because these data points are limited to a much shorter period?

As pointed out by the reviewer, the differences in variabilities shown in Figures 1 and 4 are the result of the chosen periods for the comparisons but also on the averaging of results. Figure 1 shows “smaller” variability than Figure 4 because, as described in the manuscript, the figure is based on the averages of emission factors obtained from each vehicle, whereas Figure 4 shows the comparison of individual emission factors whenever they were co-sampled by the two techniques for the same vehicle.

Technical corrections

11. p. 4, line 10: The wording "the AML was positioned behind target diesel vehicles" makes it sound like the AML was stationary or attached to the vehicles. I suggest something like, "the AML followed behind target diesel vehicles," instead.

We thank the reviewer for the suggestion, the change has been made.

12. p. 5, lines 1-2: Rewrite "we have referred rBC to BC in this manuscript

The change has been made from “…, we have referred rBC to BC in this manuscript” to: ”…, we refer to rBC as BC in this manuscript”.

13. p. 5, line 2: "detection limit" should be "detection limits".

The change has been made.

14. p. 7, line 26: Change "observed" to "reported".

The word has been changed.

Anonymous Referee #2

This is a very good paper with valuable information about diesel engine emission factors that can be used to prepare Mexican emission inventories. The experimental techniques used have been proven before and the results published in scientific journals. The paper is well written and the presentation of results is good. There are several questions I suggest to clarify before the paper is considered for publication. I enclose the reviewed file with comments and questions for your consideration. Please let me know if there is any doubt about my comments.

We thank the reviewer for the constructive comments on the paper.

P2.L12. You do not measure emission factors, you measure emissions and then estimate emission factors.

We agree with the reviewer that technically speaking the emissions factors were not directly measured but estimated from the measurements. Perhaps incorrectly, the literature on this topic traditionally does not make the explicit distinction between the two but it is left to the reader to grasp it from the description of the methodology. However, we do agree that it helps to the clarity of the discussions to explicitly refer to the results as estimations. We have modified the sentence accordingly from: "Compared to gaseous pollutants emissions, direct measurements of emission factors for PM components from diesel-powered vehicles are less abundant" to "Compared to gaseous pollutants emissions, measurement-based estimations of emission factors for PM components from diesel-powered vehicles are less abundant".

P3L21. Do you measure emission factors using a Mobile Laboratory? I think that you measured emissions and then you calculated emission factors with some uncertainty.

Based on the response to the previous comment, we have modified the corresponding sentence from:

"In this pilot study we measured the fuel-based emission factors for BC, OC, CO, NOx, and selected VOCs under real-world driving conditions for 20 on-road diesel vehicles in Mexico using the Aerodyne Research Inc. mobile laboratory (AML). The emission factors of NO, CO, HC, and fine PM were simultaneously measured using the cross-road remote sensing technique…"

To:

"In this pilot study we have estimated the fuel-based emission factors for BC, OC, CO, NOx, and selected VOCs under real-world driving conditions for 20 on-road diesel vehicles in Mexico using the Aerodyne

Research Inc. mobile laboratory (AML). The emission factors of NO, CO, HC, and fine PM were simultaneously obtained using the cross-road remote sensing technique…"

P4L114. Include a short description of the tests. Are these tests representative of driving conditions on the city?

We thank the reviewer for this valuable suggestion. We have now included a more detailed description of the driving conditions (the range of speeds and accelerations of the vehicle sampled) during the tests in the supplemental material document. Thanks to this suggestion, we believe that the results can be more adequately compared to future studies dedicated to understanding the emissions characteristics of diesel vehicles in Mexico.

To the best of our knowledge, there are no studies on the characteristics of driving cycles for diesel vehicles in Mexico and thus it is not possible to assess the representativeness of the tested driving conditions. In this pilot study we focused instead on sampling the selected vehicles in slow to medium speeds with frequent acceleration and deceleration periods as we anticipate these are common driving conditions in Mexico City routes. It is worth noting that the vehicles were driven by actual drivers from the participant institutions that volunteered their vehicles.

P6L27. Please explain this part being consistent with the definition of mass or moles. I understand that if the volume is the same, it is assumed that the mass of CO2 and CO is very large compared with the mass of other species, then the emission factor is the mass of species i/mass of carbon in CO2 and CO multiplied by the mass of carbon/mass of fuel, in this case (0.87), not the mass of CO2 and CO. The equation is correct if you use moles, but then, you need to include the molecular weight to obtain mass. You comment this for each technique, but the equation as presented is not consistent with the definitions.

The analysis methods used to obtain emission factors from the chasing and remote sensing techniques are well established and reported in detail in the references provided in the paper. As pointed out by the reviewer, the molecular weights are needed to convert from the measured gaseous species (in moles) to mass. For the AML technique we believe this is already explained in the following sentence:

"For the AML technique the gaseous species mass ratio is obtained using the moles of the pollutant and the total moles of emitted carbon by multiplying with their respective molecular weights, whereas the PM components measurements are directly obtained in μgm^{-3}, therefore the denominator units for the total carbon content need to be converted accordingly to μgCm^{-3}."

To add clarity, we have completed the last phrase as follow: "…therefore the denominator units for the total carbon content need to be converted accordingly to μgCm^{-3} using the respective CO_2 and CO molecular weights." In this way, it is clearer that for the AML technique the equation is used only after the measured (in moles) carbon content is transformed to mass.

For the application of equation 1 in the remote sensing technique, the reviewer correctly pointed out that more clarity is needed. We have expanded the sentence: “For the RS technique, the ratio is obtained from the differences in number of molecules measured before and after the sampled vehicle” to: “The RS technique measures the difference in the number of molecules of the pollutant *i* before and after the sampled vehicle passes through the detector, thus the fuel-based emission factor is estimated from the ratio of emitted *n* moles of *i* to *n* moles of CO_2 (n_i/n_{CO2}), dividing it by the sum of carbon moles in the CO_2, CO, and HC ratios to CO_2 (1, n_{CO}/n_{CO2}, and n_{HC}/n_{CO2}, respectively), and multiplying by the corresponding molecular weights and w_c.”

P6L29. What is the source of information of carbon content in diesel? Is the value in mass fraction or in mole fraction?

The value of w_c is in mass fraction. The selection of 0.87 as the carbon content in diesel fuel is a common assumption based on typical compositions that consider it as 11 to 22 carbon linear chains. PEMEX does not provide a generalized chemical formula for diesel but we consider that a good H to C ratio assumption is 1.8.

We have now clarified this by adding the words “assumed as” when referring to this value and replacing the words “weight fraction” by “mass fraction” in the sentence: “… normalized by the mass fraction carbon content of the diesel fuel w_c (assumed as 0.87) as shown in Eq. (1)”

P9.L15. In the figure it looks like the calculated values of CO EF are closer to the 1:1 ratio than the NO EF values, and I would expect a better agreement between the two techniques, but you argue the opposite. Please explain. The scale for CO data is larger than for NO data, then it is expected that the variance for CO is higher. The R2 is a comparison with respect to the mean, but I think you should be comparing with respect to a straight line with slope 1. Could you elaborate on this please?

In Figure 4 we compare individual CO and NO emission factors whenever they were obtained simultaneously by the two techniques. In the discussions of this comparison, our point is that although both techniques essentially present similar co-variability (that is, both techniques capture low and high emissions conditions) there are important differences between the results by vehicle type. The reviewer is right in that it is better to focus on the comparison of the linearity of the data. To add clarity in the text, we have replaced the discussions on the coefficient of determination for the values of the Pearson linear correlation coefficient and have added the comparison of the slope of the data to a 1:1 ratio.

As the reviewer pointed out, we argue that NO values show a linear but disperse correlation whereas CO values show less of a linear correlation (the overall Pierson coefficient for linear correlation for NO is 0.75 and slope 0.77:1 whereas the linear correlation coefficient is 0.60 for CO with a slope 0.25:1; although, as discussed in the text, both linear correlations can vary substantially by vehicle type). This is because the CO data presented in the figure is in logarithmic scale for clarity as the values can vary up to 2 orders of magnitude. Thus, we have replaced the discussion paragraph as follows:

“Whereas the overall Pearson linear correlation coefficient (R) between the two techniques is only 0.60 (slope 0.25:1) for CO, the coefficient increases to 0.96 and 0.92 for Metrobuses and service trucks, respectively. The lower CO emission factors for the UB1 high-emitter measured by the RS in comparison with the AML contributed significantly to the overall small linear correlation coefficient: R increases to 0.78 if the CO data for the UB1 is not included in the comparison. Similarly, the overall R for NO emission factors between the two techniques is only 0.75 (slope 0.77:1) but it increases to 0.86 and 0.84 for service trucks and urban buses, respectively.”

P10L29. Why turibuses are not included? Does MOVES have emission factors for turibuses?

Turibuses are not included as an explicitly vehicle category in MOVES and thus we have not used them in the comparisons.

P11L31. Describe DPF. I did not find it in the paper.

We thank the reviewer for calling our attention to this missing definition. We have now added the definitions of DPF (diesel particle filter) and selective catalytic reduction (SCR) in the text and in Table 3 where they are used.

Emission Factors of Black Carbon and Co-pollutants from Diesel Vehicles in Mexico City

Miguel Zavala[1], Luisa T. Molina[1], Tara I. Yacovitch[2], Edward C. Fortner[2], Joseph R. Roscioli[2], Cody Floerchinger[2], Scott C. Herndon[2], Charles E. Kolb[2], Walter B. Knighton[3], Victor Hugo Paramo[4], Sergio Zirath[4], José Antonio Mejía[5], Aron Jazcilevich[6]

[1]Molina Center for Energy and the Environment, La Jolla, CA, 92037, USA
[2]Aerodyne Research, Inc., Billerica, MA, 01821, USA
[3]Department of Chemistry and Biochemistry, Montana State University, MT, 59717, USA.
[4]Instituto Nacional de Ecología y Cambio Climático, Mexico City, 04530, Mexico
[5]Environmental & Transport Consultant, Mexico City, Mexico
[6]Centro de Ciencias de la Atmosfera, Universidad Nacional Autónoma de México, Mexico City, 04510, Mexico

Correspondence to: Luisa Molina (ltmolina@mce2.org; ltmolina@mit.edu)

Abstract. Diesel-powered vehicles are intensively used in urban areas for transporting goods and people but can substantially contribute to high emissions of black carbon (BC), organic carbon (OC), and other gaseous pollutants. Strategies aimed at controlling mobile emissions sources thus have the potential to improve air quality as well as help mitigate impacts of air pollutants on climate, ecosystems, and human health. However, in developing countries there are limited data on the BC and OC emission characteristics of diesel-powered vehicles and thus there are large uncertainties in the estimation of the emission contributions from these sources. We measured BC, OC and other inorganic components of fine particulate matter (PM), as well as carbon monoxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO_2), ethane, acetylene, benzene, toluene, and C2-benzenes under real-world driving conditions of 20 diesel-powered vehicles encompassing multiple emission level technologies in Mexico City with the chasing technique using the Aerodyne mobile laboratory. Average BC emission factors ranged from 0.41-2.48 g/kg-fuel depending on vehicle type. The vehicles were also simultaneously measured using the cross-road remote sensing technique to obtain the emission factors of nitrogen oxide (NO), CO, total hydrocarbons, and fine PM, thus allowing the inter-comparison of the results from the two techniques. There is overall good agreement between the two techniques and both can identify high and low emitters but substantial differences were found in some of the vehicles, probably due to the ability of the chasing technique to capture a larger diversity of driving conditions in comparison to the remote sensing technique. A comparison of the results with the US-EPA MOVES-2014b model showed that the model underestimates CO, OC, and selected VOC species whereas there is better agreement for NO_x and BC. Larger OC/BC ratios were found in comparison to ratios measured in California using the same technique, further demonstrating the need for using locally-obtained diesel-powered vehicle emission factors database in developing countries in order to reduce the uncertainty in the emissions estimates and to improve the evaluation of the effectiveness of emissions reduction measures.

1 Introduction

On-road mobile sources can substantially contribute to high emissions of black carbon (BC), organic carbon (OC), and other particulate matter (PM) components in urban areas. Although both gasoline and diesel powered vehicles are emitters of primary fine particulate matter, the available evidence indicates that when normalized to fuel consumption, PM emission factors are more than an order of magnitude higher for heavy-duty diesel vehicles compared to light-duty gasoline vehicles (e.g., Ban-Weiss et al., 2008; Dallman et al., 2014). Freight tractor trailers, public transport buses, and heavy-duty trucks are typically powered by diesel fuel due to their high requirements of power, durability, and fuel efficiency. However, diesel-power vehicles can also contribute to high levels of nitrogen oxides (NO_x), carbon monoxide (CO), volatile organic compounds (VOCs) and other harmful co-pollutants. Thus, controlling diesel-powered mobile emissions has potential to improve air quality as well as help mitigate impacts of air pollutants on climate, ecosystems, and human health.

Compared to gaseous pollutants emissions, ~~direct~~ measurement-based~~s~~ estimations of emission factors for PM components from diesel-powered vehicles are less abundant. Until recently most of the measurements of PM from diesel-powered vehicles have been obtained using either semi-quantitative opacity-based techniques or by time-integrated gravimetric measurements that are subsequently analyzed in the laboratory to estimate mass fractions of BC, OC, and other chemical PM components. In many of these studies, results are obtained using dynamometers to achieve pre-established engine-loads, standardized driving cycles, and controlled sampling conditions (e.g., Zhen et al., 2009; Cadle et al., 2009; Khalek et al., 2015). Recent technological advancements have allowed the direct measurement of BC emissions from diesel-powered vehicles under real-world driving conditions using mobile laboratories (e.g., Thornhill et al., 2010; Wang et al., 2012; Lau et al., 2015; Jezek et al., 2015), and tunnel studies (e.g., Geller et al., 2005; Ban-Weiss et al., 2008, 2009; Brimblecombe et al., 2015). Cross-road remote sensing studies and measurements obtained with on-board portable emission measurement systems (PEMS) have also been used to characterize NO_x, CO, hydrocarbons (HC), and other gaseous emissions from heavy-duty diesel vehicles (e.g., Burgard et al., 2006; Frey at al., 2008; He et al., 2010; Carslaw and Rhys-Thyler 2013).

Exhaust emissions measurements obtained using on-road or road-side mobile laboratories, traffic tunnel sampling, cross-road remote sensing, and PEMS sampling techniques vary substantially in their sampling size, sampling time, captured driving modes, and pollutants sampled. For example, traffic tunnel sampling and cross-road remote sensing studies can sample hundreds of vehicles in relatively short periods but are limited in the range of driving conditions captured. In contrast, on-road exhaust plume interception studies with mobile laboratories and PEMS can provide large amounts of information on emissions under diverse driving conditions but are often limited in their sample size. Nevertheless, the overall results from the available studies have shown that there are important differences in the emission factors obtained under real-world driving conditions when compared to dynamometer-based studies. Furthermore, recent research suggests that in-use emissions of NO_x are routinely underestimated relative to certification standards (Anenberg et al., 2017; Franco et al., 2014). The differences arise

because in real-world driving conditions there are multiple parameters (e.g., driving behavior, fuel quality, engine mechanical conditions, road conditions, etc.) that simultaneously affect the emission characteristics of on-road vehicles. These effects may not be properly captured under controlled tests (Ropkins et al., 2009). There have been some efforts to incorporate emissions and activity data obtained with PEMS into dynamometer-based tests to improve the representation of real-world driving conditions for heavy-duty diesel trucks, but there are still substantial challenges for standardizing the certification and compliance testing procedures (e.g., Zhen et al., 2009; Giechaskiel et al., 2016; Maricq et al., 2016). As mobile emission inventories should aim to accurately represent real-world driving conditions, there is a continuing need to better characterize on-road emission factors using real-world sampling techniques.

Current estimates suggest that on-road diesel vehicles are a major source of BC and other submicron carbonaceous particles in many parts of the world (Bond et al., 2013). However, the estimates are highly uncertain due to different assumptions about emission factors and the fraction of high-emitting vehicles in developing countries' fleets. In Mexico, the most recent BC emissions estimates from the 2013 greenhouse gases and black carbon emission inventory (2013 GHG-BC MNEI), suggest that on-road vehicles contribute about 25% of the total 125 Gg annual BC emissions (SEMARNAT, 2015). However, due to lack of locally obtained data, Mexico's BC and co-pollutants estimates for the diesel vehicle fleet were obtained using the default databases in the MOVES2014 EPA model (EPA, 2015) without adjusting emission factors or ancillary data. Therefore, there is a strong need to better characterize fine PM and gaseous pollutants emitted from diesel-powered vehicles in Mexico. In particular, the development of accurate emission factors and activity data for on-road vehicles is a critical step towards reducing uncertainties in Mexico's on-road emissions inventories.

In this pilot study we ~~measured~~ have estimated the fuel-based emission factors for BC, OC, CO, NO_x, and selected VOCs under real-world driving conditions for 20 on-road diesel vehicles in Mexico using the Aerodyne Research Inc. mobile laboratory (AML). The emission factors of NO, CO, HC, and fine PM were simultaneously ~~measured~~ obtained using the cross-road remote sensing technique, thus allowing the inter-comparison of the results obtained by the two techniques. The sampled vehicles included service trucks, metrobuses, turibuses, and inter-city urban buses encompassing EPA98, EPA03, EPA04, EURO3-5 emission level technologies. The results of this pilot study are useful to better understand the emission characteristics of the diesel vehicle fleet and to evaluate the emission factors used for the development of emissions inventories in Mexico, as well as to provide insights of diesel vehicle fleet emissions in other developing countries.

2 Methodology

Measurements were performed at Modulo 23, a large facility that is part of the Mexico City public transportation service (Red de Transporte de Pasajeros, or RTP), in collaboration with Mexico City Secretariat of Environment (Secretaría del Medio Ambiente, or SEDEMA) during February 25-28 of 2013, as part of the field measurement campaign to characterize the

emissions from key sources of Short-Lived Climate Forcers (SLCF-2013 Mexico). The Modulo 23 is typically used by RTP as a parking and maintenance facility for their public transport buses (see Fig. S1 in the Supplemental Material document). For this pilot project SEDEMA authorities redirected all of their scheduled RTP buses during the measurement period so that the parking area was empty and free of buses, except those selected for this study.

2.1 Sampling techniques

2.1.1 ARI mobile laboratory

The measurements were obtained using the AML by targeting on-road vehicles in "chase" and stationary road-side "exhaust plume-sampling" techniques following the procedures described in Zavala et al. (2006). Tested vehicles were driven on prescribed routes inside and outside the Modulo 23 parking facility while the AML ~~was positioned~~followed behind target diesel vehicles for continuously sampling their exhaust emissions with fast time response on-board instrumentation (see Supplemental Material document for a detailed description of driving conditions). For these on-road chase measurements the AML's velocity and acceleration were also recorded continuously as the AML trailed target vehicles sampling their exhaust plumes for a variety of driving conditions. Emissions ratios are obtained by correlating the sampled exhaust plume gaseous and particle signals with above background CO_2 and CO, which contain nearly all of pre-combustion fuel carbon. Respective amounts of exhaust plume and background pollutant concentrations are determined by comparing background levels measured just before and after each plume encounter with those inside the exhaust plumes, effectively correcting for background and providing an exhaust emission ratio that can be used to obtain fuel-based emission factors (Zavala et al., 2006).

In addition to the on-road chase technique, the AML also employed the stationary road-side exhaust plume technique consisting of positioning the mobile laboratory downwind of the sampled target vehicles' exhaust. For instance, in collaboration with SEDEMA authorities, the mobile laboratory was strategically parked in one of the city's main Bus Rapid Transit (Metrobus) passenger stations to measure the emission plumes of incoming and departing Metrobuses. Only low-speed de-accelerating and accelerating plumes were sampled at this venue. A total of 101 Metrobuses were sampled at the passenger station, encompassing multiple model years, manufacturers and engine emissions Tiers.

The measurement of vehicle emissions with the mobile laboratory is possible due to the use of high-time resolution on-board instrumentation that is capable of capturing the highly transient conditions of the sampled plumes. BC and OC were measured using a soot particle aerosol mass spectrometer (SP-AMS) developed by ARI (Onasch et al., 2012). The application of the SP-AMS for the characterization of real-world vehicle emissions has been described in detail by Dallman et al., (2014). The SP-AMS uses laser-induced incandescence of absorbing soot particles to vaporize both the coatings and black carbon cores of exhaust soot particles within the ionization region of the AMS, thus providing a high sensitivity measurement of the refractory

BC (rBC) mass and the particle's organic and inorganic coating materials (see Petzold et al., 2013). For simplicity, we ~~have~~ refer~~red~~ to rBC ~~to~~as BC in this manuscript. The detection limits in mass spectrum mode of the SP-AMS for BC and OC were 30 and 60 ng/m^3, respectively, with a nominal time resolution of 1 s. In addition to BC and OC, the SP-AMS measures other inorganic PM components including nitrates, sulfates, ammonium, and chlorides corresponding to a particle size range of 35 nm – 1 μm. In this paper, we refer to PM emission factors obtained with the mobile laboratory as the sum of BC, OC and inorganic components simultaneously measured with the SP-AMS for each sampled vehicle.

Additional instruments were deployed in the AML to characterize the gaseous pollutants of the sampled vehicles. Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometers (QC-TILDAS) were used to measure CO, SO_2, ethane (C_2H_6), and acetylene (C_2H_2), (Dallman et al., 2013). A Proton Transfer Reaction Mass Spectrometry (PTR-MS) operated using H_3O^+ as the ionization reagent (Rogers et al., 2006) was run in multiple ion detection mode to measure selected VOCs. Species measured with the PTR-MS included acetaldehyde, benzene, toluene, and C2-benzenes (sum of C_8H_{10} isomers: xylenes + ethylbenzene and benzaldehyde). Two Thermo Electron 42i chemiluminescent detectors modified for fast-response measurements of NO and NO_y and a LiCor 6262 Non-Dispersive Infrared (NDIR) instrument for CO_2 and water vapor were also used. Calibrations of these instruments were checked using certified gas standards. Other instruments on-board the mobile laboratory included a global positioning system (GPS), a sonic anemometer, and a video camera. Further details on the ARI instruments typical detection limits are presented in Table S1 of the supplemental material document.

2.1.2 Remote sensing

A remote sensing (RS) unit model 4650 developed by Environmental Systems Products was deployed in a location near the start of the prescribed routes inside the Modulo 23 (see Fig. S1 in the supplemental material document). The RS unit included both low (0.15 m) and high (3.9 m) level sampling elevations for measuring exhaust emissions, which is an important advantage when characterizing emissions from diesel-powered vehicles that have elevated tailpipes. The grade at the Modulo 23 is 0º. The location of the RS close to the start of the prescribed route was selected on the basis of obtaining an accelerating plume of the tested vehicle. Speed bar detectors were used to obtain vehicle speed and acceleration at the moment of passing through the RS unit. A video camera was placed down the road from the RS unit to take pictures of license plates when triggered.

In the RS, a NDIR exhaust gas analyzer with an optical filter of a wavelength known to be uniquely absorbed by the molecule of interest is placed in front of each detector, determining its specificity. The light source is shone across the road and reflected back. Reduction in the signal caused by absorption of light by the molecules of interest reduces the detector's signal, and thus the number of molecules of the pollutant can be inferred. The RS instrument measures CO_2, CO, total HC (as propane equivalents) using infrared light, whereas ultraviolet spectrometers are used for NO and NO_2. PM levels are not directly

measured but inferred from a "smoke factor" estimated by the manufacturer from the ultraviolet and infrared absorption (Schuchmann et al., 2010). The target gas analyzers were calibrated daily with a mixture of certified gases. Technical specifications on the accuracy of the RS unit instruments are included in Table S2 of the supplemental material document.

2.2 Vehicles sampled

Vehicles sampled in this pilot study included 9 service trucks, 4 Metrobuses, 2 Turibuses, and 5 urban (RTP) buses, encompassing models years 1995 to 2011 and EPA98, EPA04, EURO3-5 technologies (Table 1 and Fig. S2). RTP urban buses are single 2 axle vehicles used for public transport with typical capacities of 60-90 passengers. RTP urban buses typically start operations very early in the morning and are continuously driven using designated intra-city routes until nighttime when they are returned to Modulo 23 for regular maintenance, refueling, and overnight parking. Thus, RTP urban buses are continuously used throughout the day and often driven in low-speed but intense urban traffic conditions. Metrobuses are buses of one or two (merged) units that are used for transporting a large number of passengers (typical capacity is about 170 passengers) and have a dedicated (exclusive) driving lane on their route roads. The intra-city routes of Metrobuses are selected for connecting highly populated but largely separated areas in Mexico City using in-between passenger stations. Since no other vehicles are allowed to travel in the designated lanes, Metrobuses often are driven at higher speeds than the rest of the surrounding fleet and are less affected by traffic.

Turibuses are double-decker buses that take passengers on guided tours through the main touristic landmarks of the city. Turibuses are usually driven at lower speeds than the Metrobuses, with gentler driving modes, and are well maintained. The service trucks tested were medium class 7 diesel trucks used for transporting goods for Coca Cola-FEMSA. The sampled service trucks are typically driven in urban roads and are subject to intense traffic conditions. All vehicles sampled used ultra-low sulfur diesel (ULSD, < 15 ppm in S) except the Turibuses which used biodiesel with a B20 blend. All tested vehicles were ballasted in normal load operating conditions either with actual goods (for service trucks) or volunteers (for RTP buses, Metrobuses and Turibuses) during the measurements.

2.3 Data processing

Data from the ~~three~~ two sampling techniques was processed to obtain fuel-based emission factors using established analytical protocols for the ARI mobile laboratory as described in detail in Zavala et al., (2006), and for the RS measurements as described in Bishop et al., (2008). In essence, the estimation of fuel-based emission factors *EF* for the two techniques is based on obtaining the mass ratio of the species of interest, $m_{i,}$ to the total carbon mass found in above background CO_2 and CO, m_{CO2} *and* m_{CO}, respectively, (and HC in the case of RS) normalized by the ~~weight~~ mass fraction carbon content of the diesel fuel w_c (assumed as 0.87) as shown in Eq. (1):

$$EF_i = \frac{\int m_i dt}{\int (m_{CO_2} + m_{CO}) dt} w_c \quad (1)$$

For the AML technique the gaseous species mass ratio is obtained using the moles of the pollutant and the total moles of emitted carbon by multiplying with their respective molecular weights, whereas the PM components measurements are directly obtained in μgm^{-3}, therefore the denominator units for the total carbon content need to be converted accordingly to μgCm^{-3}. using the respective CO_2 and CO molecular weights. For the RS technique, the ratio is obtained from the differences in number of molecules measured before and after the sampled vehicle. The RS technique measures the difference in the number of molecules of the pollutant *i* before and after the sampled vehicle passes through the detector, thus the fuel-based emission factor is estimated from the ratio of emitted *n* moles of *i* to *n* moles of CO_2 (n_i/n_{CO2}), dividing it by the sum of carbon moles in the CO_2, CO, and HC ratios to CO_2 (1, n_{CO}/n_{CO2}, and n_{HC}/n_{CO2}, respectively), and multiplying by the corresponding molecular weights and w_c. As described above, the PM levels in the RS technique are estimated from opacity measurements using a "smoke factor" to scale the absorption reading to grams of PM/grams of fuel and thus are semi-quantitative in nature but they are useful for inter-comparing vehicle emissions within the same experiment. For all the analysis, standard temperature and pressure conditions were used.

The important differences in the data analysis for the two techniques arise with the sampling frequency and thus with the integration periods (Δt) used to calculate the emission factors. In the mobile laboratory technique, an emission factor typically is obtained from multiple individual plume periods of 5-20 s depending on the truck velocity and wind conditions following the procedures described in Zavala et al., (2006). In this pilot study, each vehicle was sampled multiple times in prescribed routes with the mobile laboratory (see sampling size in Table 1) for about 3-10 minutes each time, therefore capturing hundreds of individual plumes measurements for each vehicle. In the RS technique, the light source travels multiple times back and forth between the detectors during the short time of the passing plume of the targeted truck and the integration period is close to 1 s. Thus, the resulting estimated emission factor represents a snapshot for the driving condition at the time when the vehicle is passing through the detector.

3 Results

Table 2 shows the average and 1-standard deviation of gaseous and PM fuel-based emission factors measured with the AML and the RS techniques for each of the sampled vehicles. The table also includes the results of the emission factors measured for the Metrobuses in stationary sampling mode as described above. Since the measurements were obtained in under similar prescribed driving routes, – differences in results mainly reflect variability among vehicle engines and emission control characteristics. the results show a wide range of average emission factors associated with each vehicle engine and emission control characteristics. The large standard deviations observed reported in Table 2 indicate that most vehicles presented high variability in their emission factors under the prescribed driving routes. The urban bus UB1 was visually identified as a high

emitter during the experiments due to its intense black smoke exhaust plumes and this is confirmed by the much higher emission factors for this vehicle. Additionally, the relatively newer Dina urban bus with EURO5 technology had a malfunctioning selective catalytic reduction (SCR) device.

The average of the measured emission factors by vehicle type are shown in Fig. 1 and 2. Figure 1 shows a comparison of the CO and NO average emission factors obtained with the AML and the RS techniques whereas Fig. 2 shows the average emission factors of BC, OC, PM-inorganics, toluene, C2-benzenes, benzene, acetaldehyde, acetylene, and SO_2 measured with AML instruments. The inorganic component of PM was estimated as the sum of nitrate, sulfate, chloride and ammonium measured with the SP-AMS. For consistency in the comparisons, the emission factors shown for Metrobuses in Fig. 1 and 2 do not include data obtained in stationary sampling mode but only those obtained during the co-sampling of the two techniques. Non-paired Wilcoxon Rank test indicate that there is statistically significant difference (at the 0.05 significance level) between emission factors from service trucks, urban buses, and Metrobuses for the CO, NO_x, and SO_2 pollutants, whereas their corresponding VOCs, BC, OC, and PM-inorganic emission factors were not significantly different. VOCs, BC, and PM-inorganic emission factors from biodiesel-fueled Turibuses were significantly different from the corresponding emission factors from service trucks, urban buses, and Metrobuses.

The results show that the urban RTP buses produced the highest gaseous and PM emission factors. Conversely, the two sampled Turibuses running on biodiesel produced the lowest emission factors, particularly for BC, OC, and aromatics. The results also show that overall the emission factors measured with the remote sensing technique presented smaller variability with respect to those measured with the mobile laboratory. The higher variability observed with the mobile laboratory is likely the result of the larger range of driving conditions captured with this technique along the sampling routes, whereas the emission factors measured with the RS technique capture only the driving conditions at the time when the vehicle passes by the detectors.

Figure 3 shows a comparison of PM emission factors classified by vehicle control technology. Despite the small sampling size, the results indicate that there are marked differences between PM emissions depending on the vehicle's emissions control technology. Overall, the comparisons indicate lower PM emission factors due to improved control technology. The average PM emission factor decreases from 4.3 to 0.72 g/kg for vehicles with EURO3 to EURO5 technologies, respectively. However, the results also show that there is a large effect on the average PM emission factors when the data from the high polluting vehicle UB1 (EPA98) are included in the comparison. The average PM emission factor for the EPA98 category is reduced from 5.7 to 2.0 g/kg when the large emissions from this high-polluting vehicle are not included. Data from the single older 1995 ST7 vehicle with EPA94 technology was not included in Fig. 3 due to its relatively smaller sampling size (see Table 1). However, its average PM emission factor of 2.24 g/kg is slightly higher than the 2.0 g/kg average of the EPA98 technology excluding the high-emitting vehicle, consistent with the observed higher PM emission factors for vehicles with older technologies. Non-paired Wilcoxon Rank tests indicate that there is statistically significant difference (at the 0.05 significance

level) between the $PM_{2.5}$ emission factors obtained for the EPA98 and EPA04 control technologies as well as among the EURO3, EURO4, and EURO5 technologies. However, the results for the EPA98 and the EURO3 technologies were not significantly different.

~~The sampling size in this pilot study is too small to be a representative sample of the entire Mexican fleet. Nevertheless, there are some vehicle age and type characteristics that make the results relevant. According to the 2013 GHG BC MNEI the Mexican heavy-duty diesel fleet of about 810,000 vehicles is dominated by diesel trucks with gross vehicle weight (GVW) > 3 tons (~50.8%), followed by large trailer trucks (29.4%), urban buses (12.5%), and smaller trucks with GVW < 3 tons (4.5%) (Fig. S3 in supplemental material). Thus, the sampled service trucks, corresponding to diesel trucks with GVW>3 tons, the urban RTP buses and the Metrobuses belong to large categories of the diesel fleet. In addition, an analysis of the diesel-powered fleet distribution for Mexico City indicates that a large fraction of the in-use diesel vehicle fleet is relatively old and remains in-use for longer periods as compared to the gasoline vehicle fleet (Fig. S4 in supplement material). For example, about 61.5% and 64.9% of the buses and diesel trucks with GVW>3 tons, respectively, are older than 10 years. The vehicle model years of the sampled service trucks (1995 – 2011) correspond to about 53.4% of the diesel trucks with GVW>3 tons fleet, whereas the model years of the sampled buses are relatively newer (2002-2011) and correspond to only about 36.6% of the buses fleet.~~As shown in Figure 1, the comparison of average CO and NO emission factors by vehicle type suggests an overall good agreement between the mobile laboratory and the remote sensing techniques, particularly for NO. However, rather than comparing the averages of emission factors, a proper comparison accounting for the actual co-sampling periods between the two techniques is required. Figure 4 shows the comparison of the individual CO and NO emission factors measured for each co-sampled vehicle. Since the remote sensing technique measures the emission factor of the sampled vehicle only while it passes through the detectors, only the emission factors obtained with the mobile laboratory ~10 seconds before and up to the corresponding actual moment of co-sampling with the remote sensing detector were considered for the comparison between the two techniques. Thus, we assume that a time period of 10 seconds is sufficient to capture a large portion of the emission plume sampled by the mobile laboratory.

Figure 4 shows a linear but disperse correlation of the NO emission factors and a poor linear correlation of CO emission factors between the two techniques. Paired t-tests indicate that there is no statistical significant difference (at the 0.05 significance level) between the two measurement techniques for both cases of CO and NO_x emission factors. Arguably, the results show an overall good agreement between the two techniques in terms of their ability to distinguish low and high CO and NO emitters; however, there is some indication that the agreement varies substantially by vehicle type. Whereas the overall Pearson linear correlation coefficient (R) between the two techniques is only 0.60 (slope 0.25:1) for CO, the coefficient increases to 0.96 and 0.92 for Metrobuses and service trucks, respectively. The lower CO emission factors for the UB1 high-emitter measured by the RS in comparison with the AML contributed significantly to the overall small linear correlation coefficient: R increases to 0.78 if the CO data for the UB1 is not included in the comparison. Similarly, the overall R for NO emission factors between

the two techniques is only 0.75 (slope 0.77:1) but it increases to 0.86 and 0.84 for service trucks and urban buses, respectively. Paired t-tests indicate that there is no statistical significant difference (at the 0.05 significance level) between the two measurement techniques for both cases of CO and NO emission factors. Although the sampling size may be too small to provide a more precise quantification of the agreement between the two techniques, nevertheless, the results suggest that overall both techniques can be used to adequately distinguish between high and low emitters, but that distinction should consider the sampling efficiency by vehicle type.

4 Discussions

~~### 4.1 Comparison between measurement techniques~~

~~As shown in Figure 1, the comparison of average CO and NO emission factors by vehicle type suggests an overall good agreement between the mobile laboratory and the remote sensing techniques, particularly for NO. However, rather than comparing the averages of emission factors, a proper comparison accounting for the actual co-sampling periods between the two techniques is required. Figure 4 shows the comparison of the individual CO and NO emission factors measured for each co-sampled vehicle. Since the remote sensing technique measures the emission factor of the sampled vehicle only while it passes through the detectors, only the emission factors obtained with the mobile laboratory ~10 seconds before and up to the corresponding actual moment of co-sampling with the remote sensing detector were considered for the comparison between the two techniques.~~

~~Figure 4 shows a linear but disperse correlation of the NO emission factors and a poor linear correlation of CO emission factors between the two techniques. Arguably, the results show an overall good agreement between the two techniques in terms of their ability to distinguish low and high CO and NO emitters; however, there is some indication that the agreement varies substantially by vehicle type. Whereas the overall coefficient of determination (R^2) between the two techniques is only 0.36 for CO, the coefficient increases to 0.92 and 0.85 for Metrobuses and service trucks, respectively. The lower CO emission factors for the UB1 high emitter measured by the RS in comparison with the AML contributed significantly to the overall low correlation coefficient: not including the CO data for the UB1 in the comparison increases R^2 to 0.61. Similarly, the overall R^2 for NO emission factors between the two techniques is only 0.56 but it increases to 0.74 and 0.70 for service trucks and urban buses, respectively. Although the sampling size may be too small to provide a more precise quantification of the agreement between the two techniques, nevertheless, the results suggest that overall both techniques can be used to adequately distinguish between high and low emitters, but that distinction should consider the sampling efficiency by vehicle type.~~

4.~~2~~ 1 Comparison with MOVES2014-Mexico model

MOVES2014 is currently the most advanced model for estimating on-road emissions in the US at national, state, county, and project level as it incorporates emissions data obtained from field studies over a wide range of vehicle types, pollutants, emission processes, fuel types, and operating modes (EPA 2015). A number of studies indicate that the use of the model can improve the emissions estimates of inventories in Mexico with respect to older emission models (Zavala et al., 2013; Guevara et al., 2017). However, its efficient application to other countries requires the adjustment of multiple internal parameters, among which the emission factors databases are of key importance. A recent project was developed by the Eastern Research Group (ERG) to adjust the model's default emission factors and deterioration rates for the gasoline fleet using remote sensing data obtained in major Mexican cities (Koupal et al., 2016). The resulting model, MOVES2014-Mexico, also considers Mexican vehicle emissions and fuel quality standards, vehicle population by age and state, fuel properties and fuel consumption. However, emission factors for the diesel fleet in the model were not adjusted using field measurements data.

The heavy-duty emission exhaust database for the MOVES2014 model's previous version (MOVES2010) was originally constructed using the results of several real-world in-use dedicated studies for gaseous pollutants, including: 1) measurements of 124 trucks and buses with model years 1999 through 2007 using the Real-time On-road Vehicle Emissions Reporter (ROVER) PEMS system developed by EPA, and 2) measurements of 188 trucks with model years 1994 through 2003 using the Mobile Emissions Measurement System (MEMS) by West Virginia University (WVU). The current version of MOVES2014 builds upon these studies using two additional real-world studies: 1) the Heavy-Duty Diesel In-Use Testing (HDIU) program in which data was collected by manufacturers during normal operation for 243 diesel trucks of model years 2003-2009; and 2) the Houston Drayage Data (HDD) study in which the EPA collected emissions data from 27 trucks with model years 1991-2006 in drayage service using PEMS in the Houston-Galveston Area. Among other changes resulting from the emissions databases updates, MOVES2014 estimates higher NO_x emission factors than MOVES2010 (EPA 2015).

Databases of PM emission factors in MOVES2014 were constructed from the CRC E-55/59 research program that consisted in sampling 71 diesel vehicles with model years 1974-2004 (Clark et al., 2007). However, the PM speciation data was collected from only 9 different vehicles using the WVU's Transportable Heavy-Duty Vehicle Emissions Testing Laboratory (EPA 2014). Importantly, the measurements did not include transit buses and thus the PM emission factors for the urban bus vehicle category were proportionated using data from other measured vehicle types.

Figure 5 shows a comparison between emission factors measured with the AML and those from the MOVES2014-Mexico model in the "exhaust" emission process category. The figure compares the measured emission factors of urban buses and Metrobuses with those estimated for the Transit Bus vehicle category in the model. Measured emission factors of service trucks are compared against those estimated for the Single Unit Short-Haul Truck vehicle category in the model. Turibuses are not

included in this comparison. In addition, in the comparison only the vehicle age groups in the MOVES2014-Mexico model corresponding to those model years of the sampled vehicles are included.

The results indicate very good agreement between the modeled and measurement-based NO_x emission factors for both buses and service trucks, but suggest a significant model underestimation of CO emission factors. Model-based BC emission factors are well within the observed values for service trucks but the results show higher variability in the measurements for the urban buses and Metrobuses as compared to the model. The results also suggest a large underestimation of OC emission factors in the model for both buses and service trucks. Interestingly, despite the underestimation of OC there is a better agreement between the model and measurements for the total PM emission factor that results from a compensating effect of overestimation of the inorganic PM components in the model. The measured emission factors for acetaldehyde, benzene and toluene were all much higher than those obtained from the MOVES2014-Mexico model, consistent with the observed underestimation of CO emission factors.

Overall, the model underestimated the CO, OC, and selected VOCs but had better agreement for NO_x and BC emission factors. Due to the small sampling size in this pilot study, caution should be made when attempting to extrapolate the results from this comparison to other vehicle categories and model years. Nevertheless, the results demonstrate the need for locally adjusting the emission factors database for the diesel vehicle fleet in the MOVES2014-Mexico model using real-world driving conditions to improve the emission estimates during inventory development.

4.~~3~~ 2 Comparison with other studies

A recent study by Sheinbaum et al. (2015) investigated the impacts on PM and NO_x emission levels when using B10 and B20 biodiesel blends for 3 EPA98 and 3 EPA04 urban RTP buses in Mexico. They found mixed results on the emission benefits depending on the technology and blend composition. The average reductions of PM for the three EPA04 buses were 66% and 36% using B10 and B20 blends, whereas the corresponding reductions for NO_x where 4% and 8%. For the EPA98 buses PM increased 59% and 15% when using B10 and B20 blends, respectively, whereas NO_x correspondingly increased 8% and 3%. The two biodiesel TU1 and TU2 vehicles sampled in this study have EURO3 technology, similar to the ST4 and MT1 vehicles. Results in Table 2 show that the CO and NO_x emissions factors of the TU1 and TU2 vehicles had no distinguishable differences with respect to the ST4 and MT1 vehicles. The major difference between the biodiesel fueled vehicles and other vehicles is observed in the much smaller BC and OC emission factors. Therefore, these results also suggest PM emission reduction benefits when using the biodiesel in vehicles with newer technology.

Table 3 compares the measured BC emission factors in this study with those reported in other parts of the world obtained with various sampling techniques. In 2006, the AML measured emissions from mobile sources in Mexico City using the chase

technique and applied the positive matrix factorization (PMF) method to obtain an average fleet-wide emission factor of 1.4 g/kg for the diesel fleet (Thornhill et al., 2010). This value is well within the ranges of the measured emission factors in this study and is similar to the values obtained in Beijing and Chongqing by Wang et al. (2012). Preble et al. (2015) found much smaller BC emission factors that corresponded to newer trucks with diesel particle filters (DPF) and SCR control technologies. Our results also indicate that there is a strong effect of control technology on BC emissions. Nevertheless, the results also demonstrate that the information on the fraction of high emitters in the diesel fleet in developing countries is a key parameter for the construction of emissions inventories. In addition, the values in Table 3 indicate that there is large variability of BC emission factors measured worldwide and at different times, highlighting the need for increasing the available datasets of emission factors obtained under real-world driving conditions to improve emissions inventory accuracy.

Dallman et al. (2014) obtained an average BC emission factor of 0.62 ± 0.17 in 2010 in San Francisco using also the SP-AMS instrument and found an OC/BC ratio of 0.31 ± 0.1 for the diesel fleet. The OC/BC emission ratios in this study are much higher: 0.59, 1.19, 1.26, and 1.56 for urban buses, Metrobuses, service trucks, and Turibuses, respectively. The biodiesel Turibuses presented the larger OC/BC ratio although their BC emission factors were the smallest of all sampled vehicles. Several factors including driving conditions, vehicle technology, and diesel fuel composition can contribute to the observed differences, but the quantification of these contributions is beyond the scope of this study. Nevertheless, the~~The~~ higher organic content of the emissions in the sampled Mexican vehicles with respect to those measured in California by Dallman et al., (2014) illustrate the large emission differences in PM composition that can be found in diesel fleets around the world, thus further indicating the need for locally adjusting the emission factors databases in mobile emission models.

The sampling size in this pilot study is too small to be a representative sample of the entire Mexican fleet. Nevertheless, there are some vehicle age and type characteristics that make the results relevant. According to the 2013 GHG-BC MNEI the Mexican heavy-duty diesel fleet of about 810,000 vehicles is dominated by diesel trucks with gross vehicle weight (GVW) > 3 tons (~50.8%), followed by large trailer trucks (29.4%), urban buses (12.5%), and smaller trucks with GVW < 3 tons (4.5%) (Fig. S3 in supplemental material). Thus, the sampled service trucks, corresponding to diesel trucks with GVW>3 tons, the urban RTP buses and the Metrobuses belong to large categories of the diesel fleet. In addition, an analysis of the diesel-powered fleet distribution for Mexico City indicates that a large fraction of the in-use diesel vehicle fleet is relatively old and remains in-use for longer periods as compared to the gasoline vehicle fleet (Fig. S4 in supplement material). For example, about 61.5% and 64.9% of the buses and diesel trucks with GVW>3 tons, respectively, are older than 10 years. The vehicle model years of the sampled service trucks (1995 – 2011) correspond to about 53.4% of the diesel trucks with GVW>3 tons fleet, whereas the model years of the sampled buses are relatively newer (2002-2011) and correspond to only about 36.6% of the buses fleet.

5 Conclusions

We present the results of the measurements of fuel-based emission factors for BC, OC, CO, NO_x, and selected VOCs for diesel-powered service trucks, urban buses, Metrobuses and Turibuses in Mexico under real-world driving conditions using the AML and the remote sensing sampling techniques. The results showed higher PM emissions factors for urban buses with older technologies than for the other vehicle types and a marked dependency on vehicle emission control technology. These results further demonstrate the benefits of tighter Tier regulations and independent testing to verify the efficacy of reduced emissions standards for diesel vehicles.

The two biodiesel Turibuses presented smaller BC and OC emission factors. Although the effects from using biodiesel fuel could not be quantified in this study, the results suggest substantial emission benefits. Further dedicated studies with larger sampling size can help to quantify the benefits.

The comparison between the emission factors obtained with the two sampling techniques suggest that both techniques can be used to identify high and low vehicle emitters, but there are differences in sampling efficiency depending on the vehicle type sampled. In addition, higher variability was observed in the emission factors obtained with the mobile laboratory that likely results from the larger diversity of emission driving conditions captured with respect to the fixed-site remote sensing technique.

Comparison of the measured results with the emission factors estimated in the MOVES2014-Mexico model show that the model underestimates CO, OC, and selected VOC species but that there is better agreement for NO_x and BC. The underestimation of organic components in the model is further supported by the larger OC/BC ratios found in comparison to ratios measured elsewhere with the same sampling technique. These results further demonstrate the need to locally adjust the emission factors databases for the diesel vehicle fleet when the MOVES2014 model is applied in countries other than the US in order to reduce the uncertainty in the emissions estimates and to improve the evaluation of the effectiveness of emissions reduction measures.

Disclaimers:

The use of the MOVES2014-Mexico model in this paper is for illustrative purposes and should not be considered as an evaluation of the model's performance.

The authors declare that they have no conflict of interest.

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Table 1. Summary of sampled vehicle characteristics.

Vehicle type	Vehicle ID	Make	Model year	Tier	Sampling size[1]	
					AML	RS
Service truck	ST1	Freightliner	1998	EPA98	22	3
	ST2	Freightliner	1998	EPA98	21	7
	ST3	International	2011	EPA04	14	6
	ST4	Freightliner	2006	EURO3	15	4
	ST5	HINO	2011	EURO4	14	4
	ST6	Kenworth	2010	EPA04	15	4
	ST7	Mercedes-Benz	1995	EPA94	4	4
	ST8	Freightliner	1999	EPA98	9	3
	ST9	Freightliner	1999	EPA98	8	3
Urban bus	UB1	International	2002	EPA98	38	8
	UB2	International	2009	EPA04	21	6
	UB3	Mercedes- Benz	2002	EPA98	29	6
	UB4	Mercedes- Benz	2009	EPA04	9	6
	UB5	Dina	2013	EURO5	15	15
Metrobus	MT1	Scania	2005	EURO3	9	5
	MT2	Volvo	2009	EURO4	9	8
	MT3	Mercedes- Benz	2011	EURO5	10	13
	MT4	Volvo	2012	EURO5	6	8
Turibus	TU1	Scania	2006	EURO3	6	5
	TU2	Scania	2002	EURO3	8	5

[1]Sampling size refers to the number of emission factors obtained with the mobile laboratory (AML) and remote sensing (RS) unit from the prescribed routes. See text for explanation of the sampling periods for each technique.

Table 2. Measured on-road average fuel-based emission factors (g/kg fuel) ~~measured~~.[1]

ID	CO		NO		NO_x[6]	HC[5]	SO_2	C_2H_2	C_2H_4O	Benzene	Toluene	C2-B[2]	BC	OC	Inorg[2]	PM[3]
	AML	**RS**	**AML**	**RS**	**AML**	**RS**	**AML**	**AML**	**AML**	**AML**	**AML**	**AML**	**AML**	**AML**	**AML**	**RS**
ST1	24.3 (15)	17.1 (1)	13.5 (3)	12.5 (1)	23.4 (5)	0.8 (0.2)	0.16 (0.1)	0.12 (0.1)	0.15 (0.1)	0.16 (0.2)	0.24 (0.2)	0.23 (0.2)	0.59 (0.5)	0.88 (0.8)	0.14 (0.1)	2.45 (0.6)
ST2	20.3 (10)	15.2 (5)	11.4 (3)	9.8 (1)	19.7 (3)	2.0 (1.1)	0.16 (0.1)	0.06 (0.03)	0.17 (0.1)	0.10 (0.04)	0.21 (0.1)	0.19 (0.1)	2.01 (1.4)	1.49 (0.7)	0.04 (0.01)	3.17 (1.1)
ST3	17.0 (9)	11.1 (1)	24.9 (20)	14.2 (1)	36.1 (8)	2.5 (0.9)	0.40 (0.2)	0.05 (0.04)	0.24 (0.1)	0.12 (0.1)	0.23 (0.2)	0.31 (0.4)	0.71 (0.6)	1.05 (1.3)	0.09 (0.05)	1.3 (0.2)
ST4	32.8 (18)	23.4 (4)	33.8 (25)	35.8 (5)	45.5 (14)	8.0 (1.3)	0.72 (0.4)	0.12 (0.1)	0.49 (0.7)	0.26 (0.3)	0.58 (0.8)	0.52 (0.8)	0.96 (0.5)	1.11 (0.6)	0.11 (0.03)	2.06 (0.6)
ST5	61.9 (17)	78.8 (7)	11.5 (3)	13.8 (3)	17.6 (3)	2.5 (0.6)	0.63 (0.1)	0.18 (0.06)	0.54 (0.1)	0.18 (0.1)	0.30 (0.2)	0.25 (0.1)	0.72 (0.6)	0.85 (0.4)	0.06 (0.01)	3.04 (0.4)
ST6	22.0 (24)	15.4 (5)	16.1 (3)	18.5 (7)	29.2 (6)	2.5 (0.6)	0.43 (0.1)	0.08 (0.1)	0.37 (0.3)	0.18 (0.1)	0.38 (0.3)	0.30 (0.2)	0.74 (0.7)	0.92 (0.6)	0.06 (0.01)	2.11 (0.6)
ST7	23.1 (3)	23.6 (7)	18.4 (4)	18.0 (2)	28.9 (6)	21.4 (3.1)	0.35 (0.1)	0.11 (0.03)	0.50 (0.2)	0.13 (0.04)	0.18 (0.1)	0.20 (0.02)	0.14 (0.1)	2.07 (0.2)	0.03 (0.01)	4.15 (0.8)
ST8	26.7 (4)	26.2 (3)	11.8 (2)	13.1 (1)	21.9 (6)	2.4 (1.7)	0.42 (0.2)	0.11 (0.03)	0.26 (0.1)	0.12 (0.03)	0.22 (0.1)	0.18 (0.1)	0.40 (0.2)	0.80 (0.2)	0.03 (0.01)	2.28 (0.4)
ST9	33.8 (13)	14.3 (5)	14.9 (8)	14.8 (5)	21.0 (6)	3.5 (0.6)	0.51 (0.2)	0.12 (0.1)	0.38 (0.3)	0.21 (0.2)	0.65 (0.9)	0.39 (0.4)	2.19 (1.6)	1.50 (0.8)	0.08 (0.01)	2.3 (0.4)
UB1	140.3 (131)	34.3 (15)	11.9 (5)	10.1 (2)	21.4 (7)	5.2 (3.9)	0.47 (0.4)	0.39 (0.3)	0.34 (0.2)	0.30 (0.2)	0.60 (0.7)	0.58 (0.7)	10.37 (11.6)	4.50 (2.8)	0.10 (0.03)	11.45 (2.6)
UB2	23.5 (13)	17.4 (14)	20.3 (8)	21.1 (4)	39.9 (8)	5.4 (6.5)	0.21 (0.1)	0.08 (0.04)	0.23 (0.1)	0.13 (0.1)	0.23 (0.1)	0.21 (0.1)	0.30 (0.9)	0.55 (0.7)	0.04 (0.01)	2.32 (1.8)
UB3	33.6 (15)	17.2 (4)	18.0 (7)	17.1 (4)	28.8 (10)	4.4 (2.8)	0.24 (0.4)	0.08 (0.03)	0.36 (0.4)	0.14 (0.1)	0.23 (0.2)	0.28 (0.3)	1.01 (1.4)	0.85 (0.6)	0.05 (0.02)	1.77 (0.7)
UB4	23.4 (10)	19.4 (9)	18.2 (5)	21.9 (6)	31.2 (8)	0.5 (0.1)	0.12 (0.1)	0.05 (0.03)	0.15 (0.04)	0.10 (0.03)	0.13 (0.1)	0.13 (0.1)	0.58 (0.2)	0.88 (0.3)	0.04 (0.01)	2.44 (1.1)
UB5	28.6 (14)	15.3 (6)	32.8 (7)	35.8 (6)	58.9 (7)	6.0 (4.3)	0.41 (0.1)	0.05 (0.02)	0.17 (0.1)	0.11 (0.1)	0.27 (0.2)	0.17 (0.1)	0.12 (0.1)	0.57 (0.4)	0.06 (0.02)	1.17 (0.7)
MT1	35.6 (14)	30.0 (11)	15.4 (2)	17.6 (3)	29.0 (2)	10.7 (6.2)	0.16 (0.1)	0.09 (0.03)	0.18 (0.04)	0.13 (0.03)	0.19 (0.1)	0.18 (0.1)	3.64 (1.7)	4.15 (1.8)	0.03 (0.01)	4.08 (1.2)
MT2	67.5 (57)	32.9 (40)	18.3 (4)	24.6 (10)	31.8 (5)	2.4 (1.3)	0.25 (0.1)	0.08 (0.03)	0.26 (0.1)	0.17 (0.1)	0.37 (0.2)	0.33 (0.1)	0.82 (0.4)	0.91 (0.3)	0.06 (0.01)	0.73 (0.5)
MT3	43.6 (23)	24.9 (16)	21.1 (4)	21.5 (5)	37.0 (6)	0.3 (0.1)	0.22 (0.1)	0.17 (0.1)	0.26 (0.1)	0.14 (0.05)	0.90 (0.3)	0.29 (0.1)	0.27 (0.2)	0.44 (0.1)	0.03 (0.01)	1.75 (0.9)
MT4	7.8 (5)	28.4 (25)	14.3 (3)	12.7 (4)	22.6 (4)	6.0 (7.3)	0.13 (0.03)	0.06 (0.02)	0.16 (0.04)	0.07 (0.02)	0.15 (0.04)	0.12 (0.04)	0.23 (0.1)	0.40 (0.1)	0.03 (0.01)	2.21 (1.6)
MTs[4]	53.9 (44)		13.5 (5)		21.2 (8)		0.18 (0.2)	0.20 (0.2)	0.51 (0.7)	0.27 (0.3)	0.50 (0.5)	0.40 (0.4)	0.99 (1.2)	0.84 (0.7)	0.14 (0.04)	
TU1	24.1 (7)	33.2 (17)	19.0 (5)	21.9 (3)	29.1 (6)	12.7 (4.0)	0.06 (0.03)	0.16 (0.1)	0.27 (0.1)	0.09 (0.01)	0.16 (0.1)	0.16 (0.1)	0.07 (0.02)	0.50 (0.05)	0.04 (0.01)	3.6 (1.5)
TU2	22.1 (11)	36.1 (12)	16.1 (4)	15.5 (2)	26.7 (6)	3.0 (0.7)	0.17 (0.08)	0.06 (0.04)	0.23 (0.1)	0.08 (0.01)	0.12 (0.04)	0.11 (0.03)	0.76 (0.8)	0.78 (0.3)	0.04 (0.01)	5.03 (1.8)

[1]Numbers in parenthesis represent standard deviations. AML and RS stand for mobile laboratory and remote sensing techniques. Vehicle identification codes can be found in Table 1.

[2] C2-B correspond to the sum of C_8H_{10} isomers. "Inorg" represents the sum of ammonium, chloride, sulfates, and nitrate measured with the SP-AMS.

[3] PM from remote sensing are obtained from a "smoke factor" applied to absorption measurements.

[4] MTs represent the measurements obtained in stationary mode for ~~hundredths~~ 101~~of~~ Metrobuses. See text for further details.

[5] Total HC emission factors expressed as propane equivalents.

[6] NO_x emission factors from the AML are expressed as NO_2-equivalents

Table 3. Comparison of measurements of BC emission factors from diesel-powered sources.

Location and sampling year	Source type	Sampling technique	Mean and SD [g/kg-fuel]	Reference
Mexico City, 2013	Turibus	Chasing	0.41 ± 0.7	This study
Mexico City, 2013	Metrobus	Chasing	1.24 ± 1.8	This study
Mexico City, 2013	Urban bus	Chasing	2.48 ± 7.3	This study
Mexico City, 2013	Service trucks	Chasing	0.94 ± 1.1	This study
Los Angeles, 1997	HDDV	Tunnel	1.3	Kirchstetter et al., 1999
San Francisco, 2005	MDDT,HDDV	Tunnel	0.78 ± 0.09	Geller et al., 2005
San Francisco, 1997, 2006	MDDT, HDDV	Tunnel	0.92 ± 0.07	Ban-Weiss et al., 2008
Mexico City, 2006	Diesel fleet	Chasing[c]	1.4 (1.3-1.6)[a]	Thornhill et al., 2010
San Francisco, 2006	HDDV	Tunnel	1.7 ± 2.3	Ban-Weiss et al., 2009
Wilmington, CA, 2007	HDDT	Chasing[c]	0.5 (0.07–0.1)[b]	Park et al., 2011
Beijing, 2009	HDDT	Chasing	2.2 (0.4-1.7)[a]	Wang et al., 2012
Chongqing, 2010	HDDT	Chasing	1.6 (0.7-1.6)[a]	Wang et al., 2012
Beijing, 2010	HDDT	Chasing	1.1 (0.2-0.8)[a]	Wang et al., 2012
San Francisco, 2010	HDDT	Tunnel	0.62 ± 0.17	Dallman et al., 2014
Los Angeles, 2011	HDDV freeways	Chasing[c]	1.33 ± 0.33	Hudda et al., 2013
Slovenia, 2011	Buses	Chasing	0.4 (0.24–0.65)[b]	Jezek et al., 2015
Oakland, CA, 2011-2013	HDDT	Tunnel	1.15 ± 0.19 0.09 ± 0.04	Preble et al., 2015[d]
Hong Kong, 2013-2014	HDDV	Chasing	2.2 ± 0.3	Lau et al., 2015
Hong Kong, 2014	Diesel fleet	Tunnel	1.28 ± 0.76	Brimblecombe et al., 2015

[a] Represent average and 1st and 3rd quartiles of data.

[b] mean and 95% confidence interval. HDDT: Heavy-duty diesel vehicle; HDDT: Heavy-duty diesel truck; MDDT: Medium-duty diesel truck.

[c] Includes chasing and fleet average values.

[d] sampling of individual plumes on an overpass. High BC value represents 2009 fleet with 2% diesel particle filters (DPF) and 0 % selective catalytic reduction (SCR) installed, whereas low BC value represents 2010-2013 trucks with full DPF and SCR systems installed.

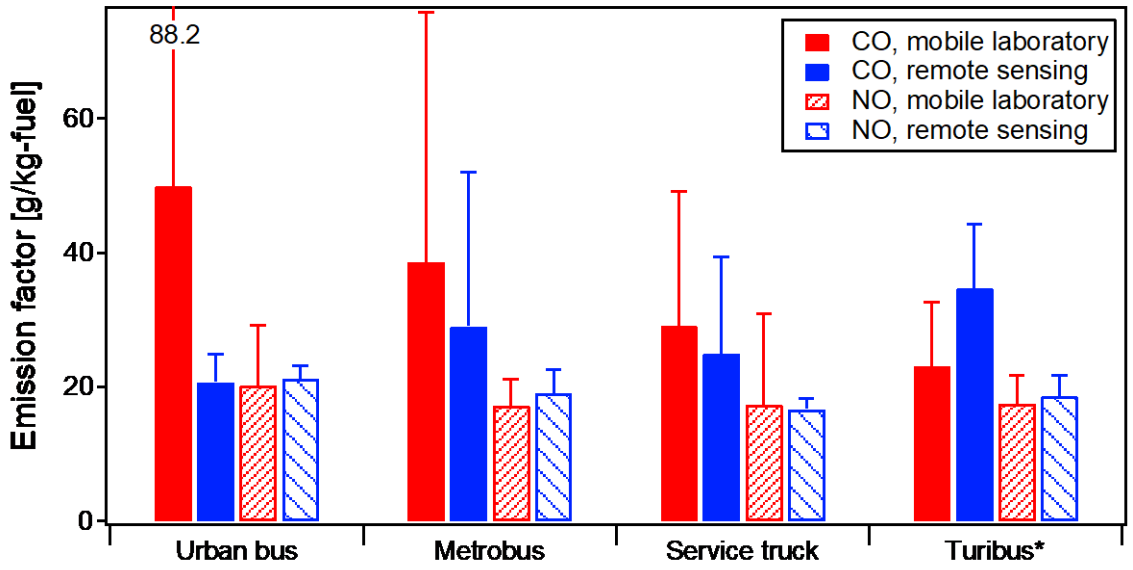

Figure 1: Comparison of average fuel-based emission factors (g/kg fuel) between the mobile laboratory and remote sensing techniques by vehicle type. Variability bars represent 1 standard deviation of the observed values.* Turibuses are fueled by biodiesel B20.

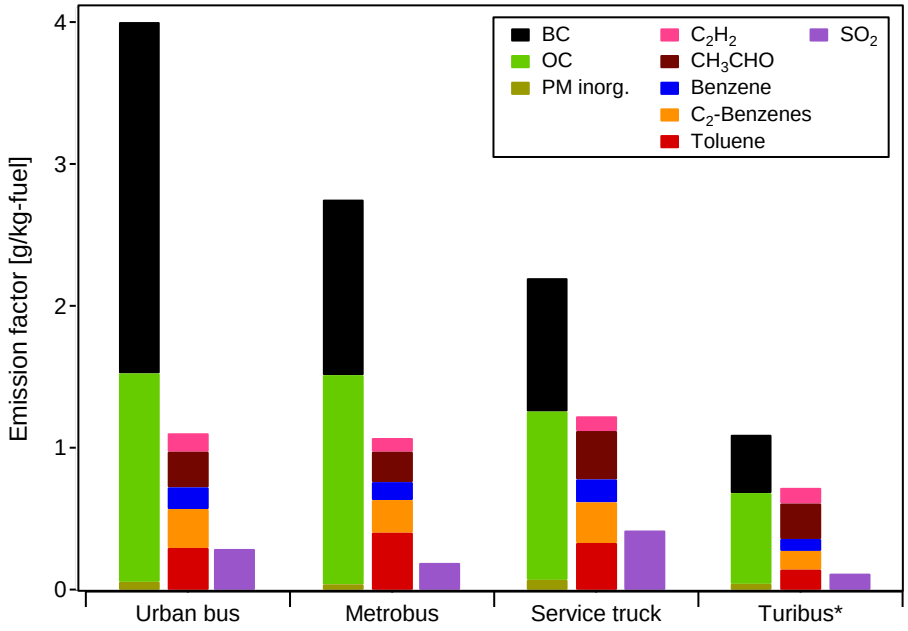

Figure 2: Comparison of average VOCs, PM components, and SO2 fuel-based emission factors (g/kg fuel) measured with the mobile laboratory by vehicle type. PM Inorganics refers to the sum of ammonium, chloride, sulfates, and nitrate measured with the SP-AMS.* Turibuses are fueled by biodiesel B20.

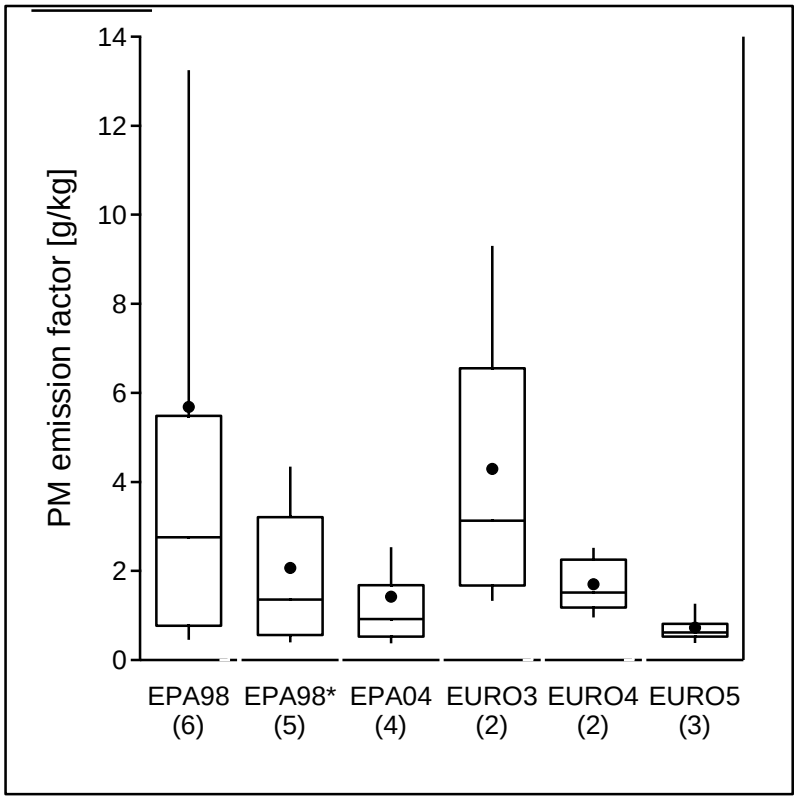

Figure 3: Box plots of PM emission factors measured by control technology. The numbers in parenthesis represent the number of sampled vehicles. Upper vertical central lines, upper level box lines, middle horizontal lines, lower box lines, and lower vertical central lines represent 90%, 75%, 50%, 25%, and 10% of the data. The first box plot of the EPA98 technology category includes the high emitter vehicle UB1 (see Table 2) whereas the adjacent box plot does not include this vehicle. PM was obtained as the sum of BC, OC, chlorides, ammonium, sulfates, and nitrates components measured by the SP-AMS.

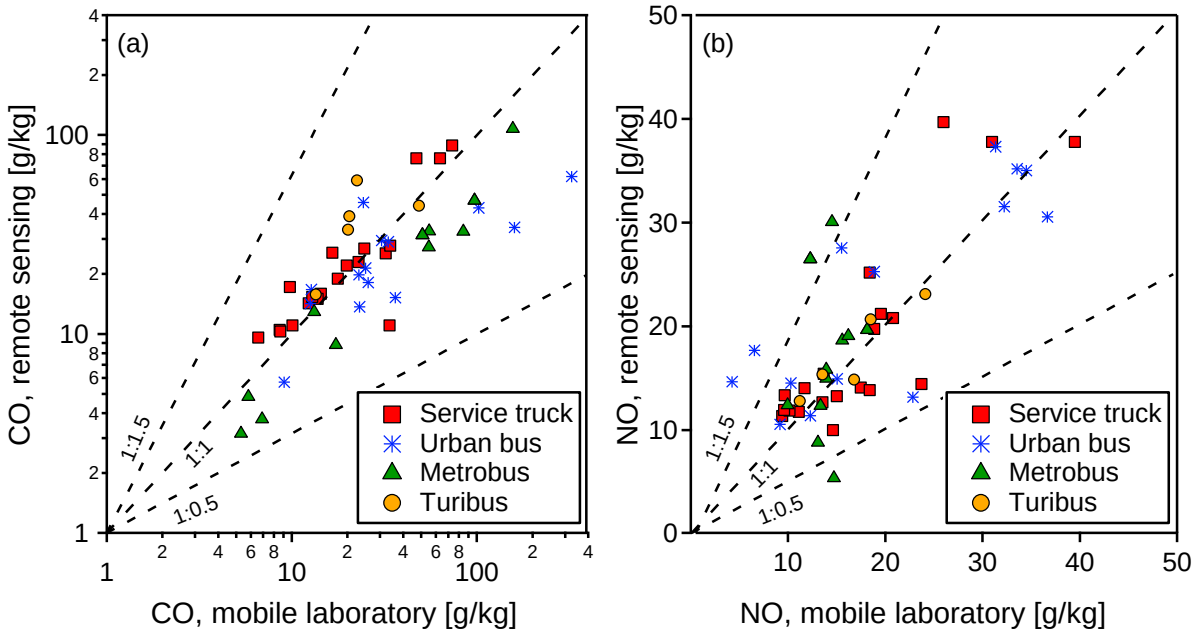

Figure 4: Comparison of (a) CO and (b) NO fuel-based emission factors measured with the mobile laboratory and remote sensing techniques. Dashed lines represent 1:1.5, 1:1, and 1:0.25 lines.

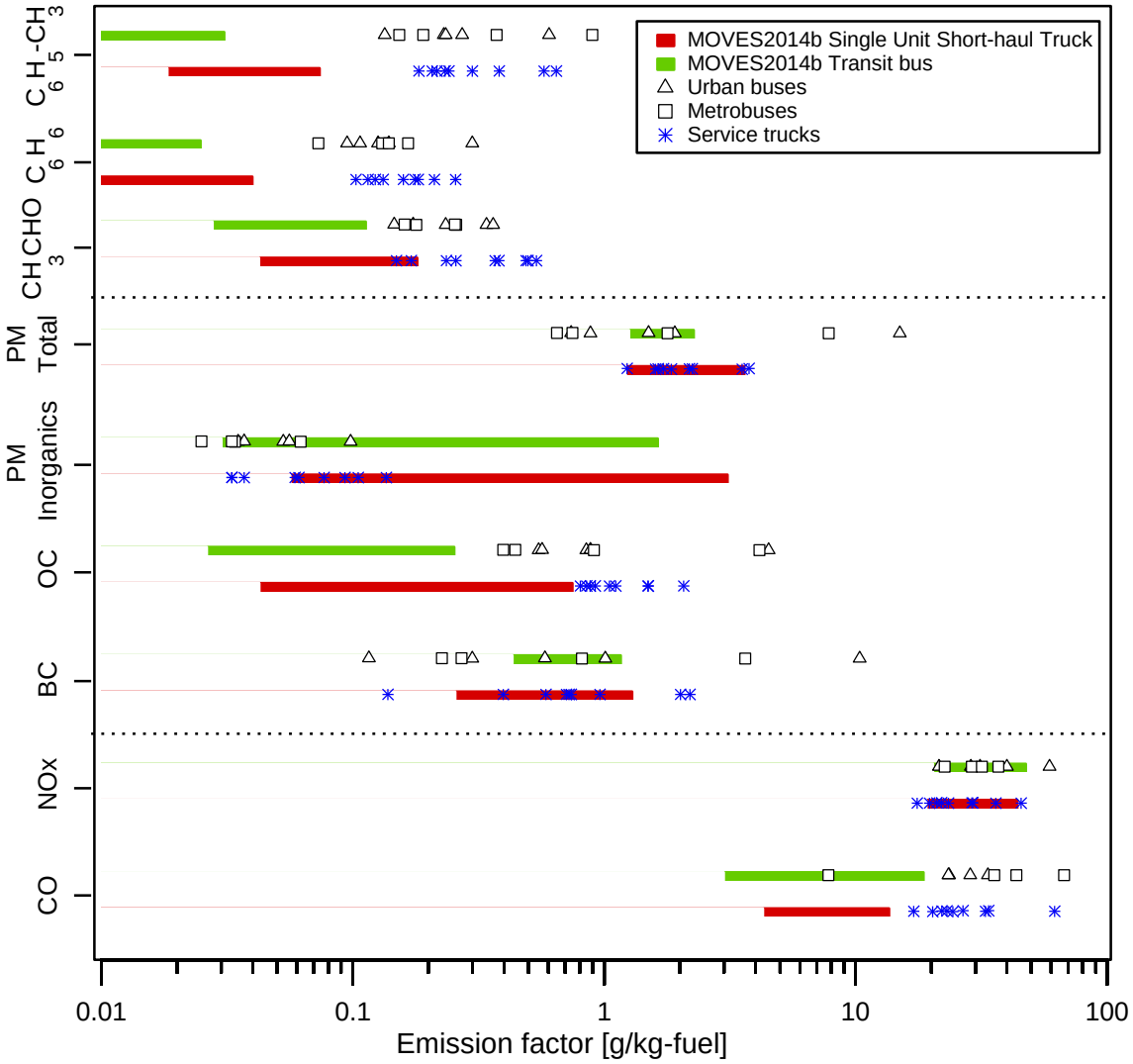

Figure 5: Comparison between AML measurements and MOVES2014-Mexico emission factors.

Emission Factors of Black Carbon and Co-pollutants from Diesel Vehicles in Mexico City

Miguel Zavala[1], Luisa T. Molina[1], Carl Cman[2], Tara I. Yacovitch[2], Edward C. Fortner[2], Joseph R. Roscioli[2], Cody Floerchinger[2], Scott C. Herndon[2], Charles E. Kolb[2], Walter B. Knighton[3], Victor Hugo Paramo[4], Sergio Zirath[4], José Antonio Mejía[5], Aron Jazcilevich[6]

[1]Molina Center for Energy and the Environment, La Jolla, CA, 92037, USA
[2]Aerodyne Research, Inc., Billerica, MA, 01821, USA
[3]Department of Chemistry and Biochemistry, Montana State University, MT, 59717, USA.
[4]Instituto Nacional de Ecología y Cambio Climático, Mexico City, 04530, Mexico
[5]Environmental & Transport Consultant, Mexico City, Mexico
[6]Centro de Ciencias de la Atmosfera, Universidad Nacional Autónoma de México, Mexico City, 04510, Mexico

Supplemental Material

This Supplemental Material document contains additional information on the instrumentation deployed, a description of the driving conditions during the measurement of emissions from the selected on-road vehicles, as well as additional figures and tables that are discussed in the manuscript.

1. Instruments on-board the Aerodyne Mobile laboratory

Tables S1 and S2 show the characteristics of the instruments deployed by the ARI mobile laboratory and the remote sensing unit, respectively, during the on-road measurements.

Table S1. Characteristics of instruments deployed by the ARI mobile laboratory.

Instrument	Pollutants measured	Detection limit by pollutant
Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometers (QC-TILDAS)	Carbon monoxide (CO) and nitrous oxide (N_2O); ethane (C_2H_6); methane isotopes ($^{13}CH_4$ and $^{12}CH_4$), sulfur dioxide (SO_2), and acetylene (C_2H_2).	Typical detection limits are 0.1 ppbv in 1-s, each of the pollutants quantified in this work is detected in plume encounters well above the detection limit.
Proton Transfer Reaction Mass Spectrometer (PTRMS)	Oxygenates, aromatics.	Typical detection limits are 0.3 – 0.8 ppbv depending on compound in 1-s of integration time.
Soot Particle Aerosol Mass Spectrometer (SP-AMS)	70 nm – 1.5 µm aerodynamic diameter aerosol, composition resolved into black carbon; sulfate; nitrate; ammonium; chloride and organic PM.	300 ng/m^3 in 1-s integration time.
Thermo Electron 42i chemiluminescent detector	NO, NO_y	0.4 ppbv in 1-s integration time for each species.
LiCor 6262 Non-Dispersive Infrared (NDIR)	CO_2	300 ppb in 1-s integration time. Plume enhancements in excess 5 ppm were quantified.

Table S2. Characteristics of instruments deployed by the Remote Sensing (RS) unit.

Pollutants measured	Detection limit by pollutant
[1]CO_2 plume> 20%-cm	
CO [%]	±0.1 or ±10% of reading, whichever is greater
HC (as propane) ppm	±100 or ±10% of reading, whichever is greater
NO [ppm]	±150 or ±10% of reading, whichever is greater
Smoke number[2]	±0.05 or ±10% of reading, whichever is greater
[1]CO_2 plume< 20%-cm	
CO [%]	±0.15 or ±15% of reading, whichever is greater
HC (as propane) ppm	±150 or ±15% of reading, whichever is greater
NO [ppm]	±225 or ±15% of reading, whichever is greater
Smoke number[2]	±0.1 or ±15% of reading, whichever is greater

[1]Static background conditions and mean value. Source: RSD4600 NextGen Operator's Manual. Edition 1.0. Environmental Systems Products. 4-000-MAN1160.
[2] Units are ~ grams diesel particulate per 100 gram fuel.

2. Sampling driving conditions

To the best of our knowledge, there are no studies on the characteristics of driving cycles for diesel vehicles in Mexico and thus it is not possible to assess the representativeness of the tested driving conditions. In this pilot study we focused instead on sampling the selected vehicles in slow to medium speeds with frequent acceleration and deceleration periods as we anticipate these are common driving conditions in Mexico City routes.

The selected vehicles were sampled using similar driving conditions by following the same route and driving under similar ranges of speeds and accelerations multiple times. The vehicles engines were previously warmed up before each measurement, and thus the measurements do not represent cold-start emissions conditions. In addition, all RTP buses, Metrobuses and Turibuses vehicles were sampled in full load capacity with the kind collaboration of volunteer students (an exception was the single DINA bus sampled, which was ballasted using filled water cans), whereas service trucks were ballasted with actual goods provided by the participating institutions. The sampled vehicles were driven by actual drivers from the corresponding participant institutions.

As described in the main manuscript, a global positioning system (GPS) was used on-board the mobile laboratory to obtain the spatial coordinates during the study. Since the measurements are obtained in vehicle "chase" mode, at a first approximation these data can be used to describe the speed and acceleration driving conditions. The average time for a given driving cycle was of 3.3 minutes with an average speed of 5.5 m/s. To assess the fraction of the time that the measurements are obtained in acceleration, deceleration, or cruising modes it is necessary to define a speed change criteria over the GPS data acquisition time (1 second). Following the

procedure of Tong et al (2000) we have defined the acceleration, deceleration, and cruising modes as follow:

1) Acceleration mode: positive incremental speed changes of more than 0.1 m/sec/sec during the 1-second interval.
2) Deceleration mode: negative incremental speed changes of more than to 0.1 m/sec/sec during the 1-second interval.
3) Cruising mode: absolute incremental speed changes of less than or equal to 0.1 m/sec/sec during the 1-sec interval.

The resulting driving cycle distribution is shown in Table S3.

Table S3. Summary characteristics of sampling driving cycles.

Mode	% of time
Acceleration	22.3
Deceleration	34.8
Cruising	29.1
Idling	13.8

Reference:
H.Y. Tong, W.T. Hung & C.S. Cheung (2000) On-Road Motor Vehicle Emissions and Fuel Consumption in Urban Driving Conditions, Journal of the Air & Waste Management Association, 50:4, 543-554, DOI: 10.1080/10473289.2000.10464041.

3. Additional figures

The following figures are discussed in the text of the manuscript. As a note, the emissions of CO, NO_x, HC and PM for a Dina vehicle were further co-sampled using an AXION PEMS instrument (see Figure S1). Therefore, for this vehicle the chasing, cross-road remote sensing, and PEMS techniques were applied simultaneously. However, the results of the inter-comparison of the three techniques are not included in this manuscript but are discussed in separate publication.

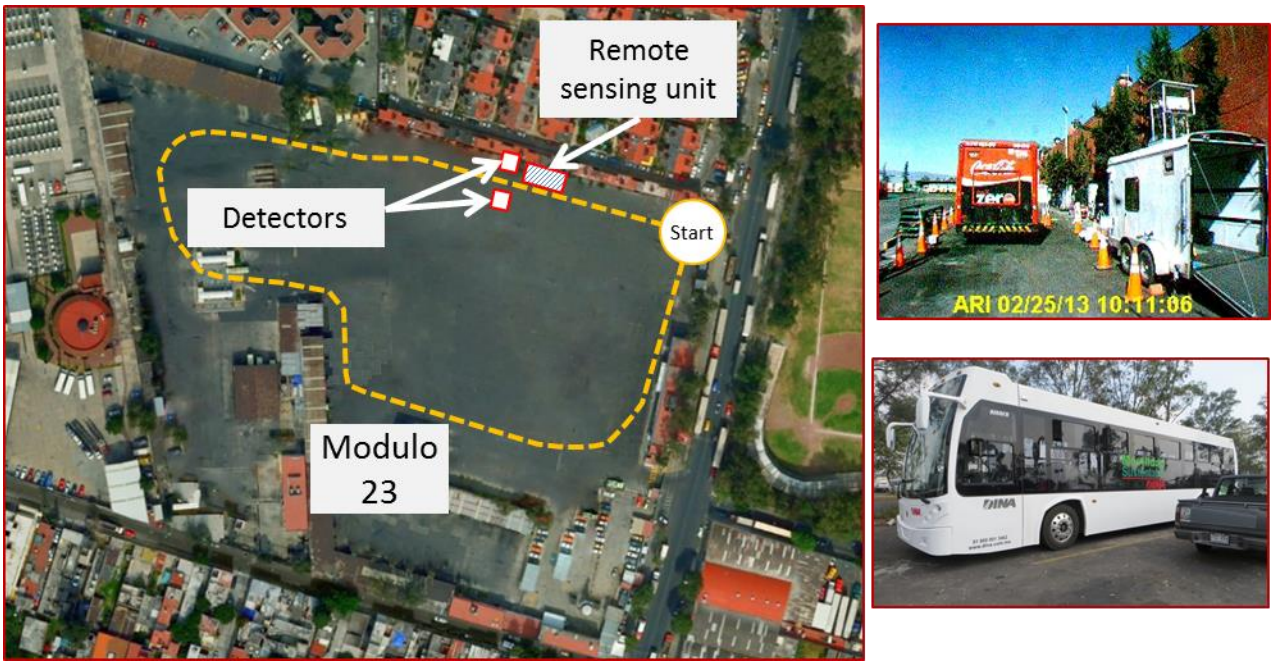

Figure S1 Top figure shows an aerial photo of the Modulo 23 of the RTP facilities with an indication of the location of the remote sensing unit and the area for the chasing experiments. Photos on the right show a service truck passing through the remote sensing detectors unit (top-right photo) and the Dina bus sampled with the mobile laboratory, remote sensing and PEMS techniques.

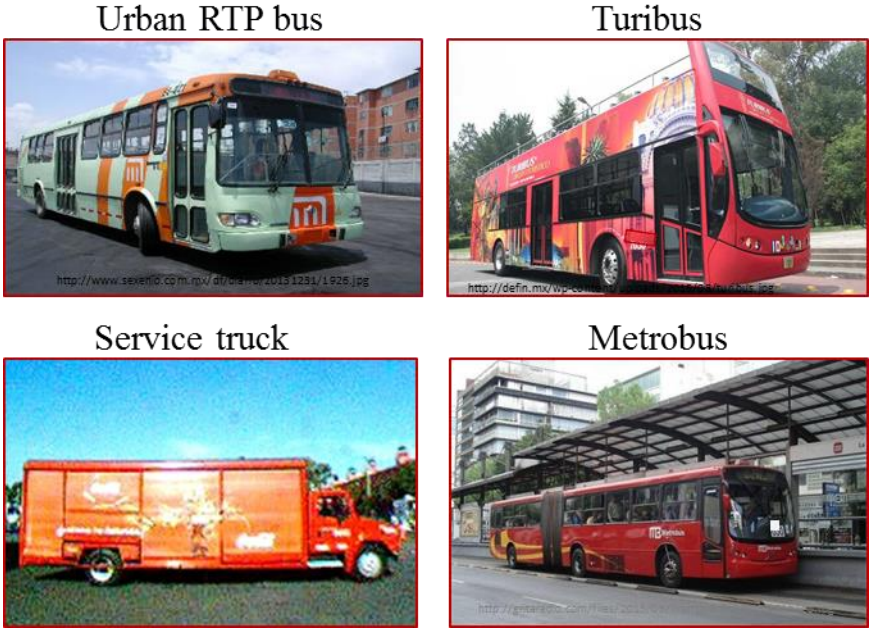

Figure S2. Examples of the four vehicle types (Metrobus, Turibus, urban RTP bus, and service truck) sampled in this pilot study.

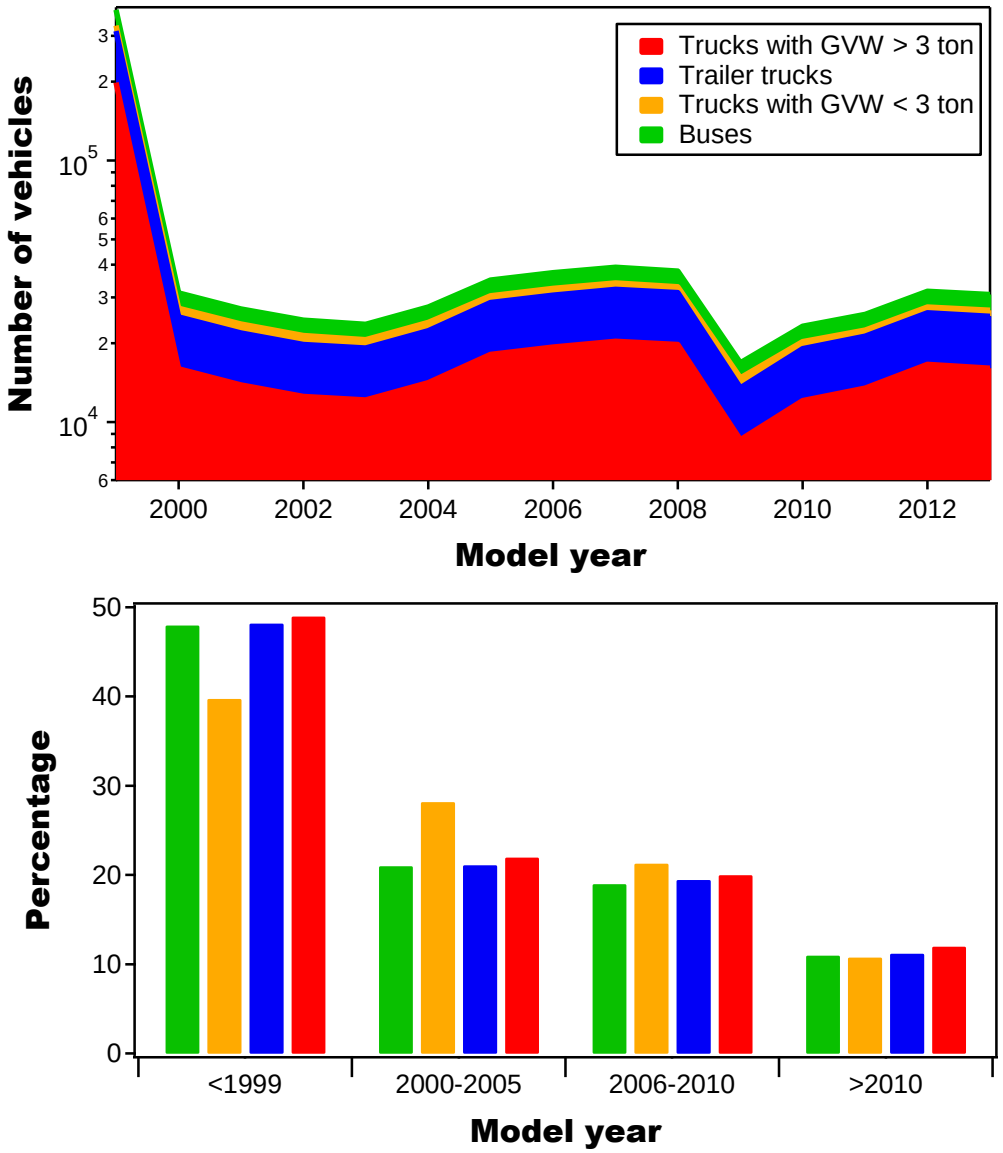

Figure S3. Top panel shows the number of diesel-powered vehicles by model year for the Mexican fleet for the year 2013. Trucks are classified by gross vehicle weight (GVW). Bottom panel shows the corresponding percentage of the number of diesel powered vehicles by model year. Source: prepared from data from the 2013 Mexican Nacional Emissions Inventory (SEMARNAT, 2015).

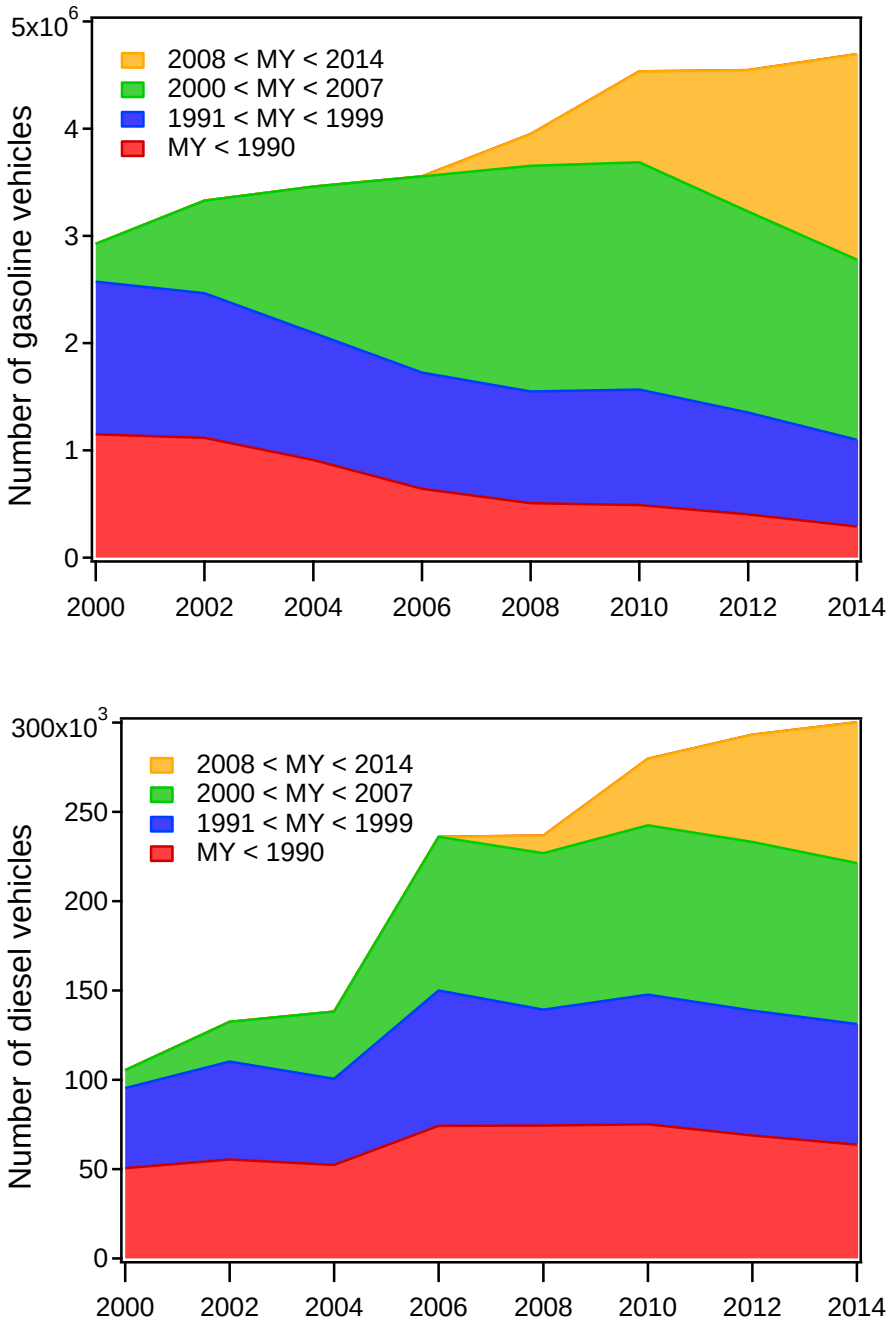

Figure S4. Top and bottom panels show the time evolution of number of gasoline-powered vehicles and diesel-powered vehicles, respectively, by model year (MY) in Mexico City. The figure shows a more rapid decline in the number of older gasoline vehicles than of diesel vehicles. Thus, older diesel vehicles remain in-use in the fleet for much longer periods than the gasoline vehicles. Source: prepared from data from the 2014 Mexico City Metropolitan Area Emissions Inventory (SEDEMA, 2017).